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RELATION OF pH AND OXIDATION POTENTIAL TO SEDIMENTARY IRON MINERAL FORMATION.

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ABSTRACT.

This paper reports the results of a series of experiments performed to test the validity of the theoretical relations among several iron minerals. Equilibrium diagrams are drawn showing stability fields of hematite, siderite, and pyrite as functions of pH and oxidation potential for various low temperature environments, such as sea water or other relatively dilute salt solutions. The experiments show that ferric hydroxide (ferric oxide) comes to equilibrium with its environment in a few hours, ferrous carbonate requires several weeks, but reacts at an easily detectable rate; ferrous sulfide is not formed in detectable quantities over a period of several weeks by a change from an oxidizing to a reducing environment in an inorganic system. Ferrous hydroxide is easily precipitated from deoxygenated solutions; it oxidizes very rapidly to ferric hydroxide in air. The theoretical and empirical chemical relations of these iron compounds seem applicable to natural conditions; observed iron mineral associations have a reasonable interpretation within this framework. The work indicates that iron, if transported in solution to the site of deposition, is carried in mildly acid waters, and that any deficiency in aeration of these waters contributes further to iron solubility. Another implication is that the accumulation of thick layers of iron-rich rocks requires a trap between the source of iron and the depositional area if associated clastics are to be removed from iron-rich waters.

INTRODUCTION.

THE origin of the sedimentary iron formations is a problem with many unsolved aspects. Among them are the nature of the terrain from which the iron was derived; the conditions of weathering under which the iron was released; the form of the iron during transport—whether in true solution or colloidal suspension; the mechanism of separation of the iron from associated materials in transport; the controls of the mineral species in which the iron was deposited; and the reasons for the association of these species with particular non-ferrous minerals.

The geologic environment of formation of the Clinton type hematitic iron deposits has been admirably deciphered (especially Alling, 2).[1] These deposits were laid down in a series of well aerated shallow basins. Using Alling's work as their chief guide for conditions of deposition of the Clinton deposits, Castaño and Garrels (3) attacked the problem of iron transportation and precipitation both theoretically and experimentally, making the basic assumption that iron is transported in true solution. They showed on theoretical grounds that in oxygenated waters sufficient iron could be carried in slightly acid rivers to form large iron deposits, and that the iron should be precipitated as ferric oxide where these rivers mixed with typical marine waters in equilibrium with calcium carbonate. Experiments in which a river was simulated by a dilute iron chloride solution, and a sea by a salt solution containing excess solid calcium carbonate, showed that the theoretical predictions, based on equilibrium chemical relations, were realized in the laboratory. Because equilibrium was attained in the experimental system, even though the experiments lasted only a few hours or days, the conclusion seemed warranted that equilibrium would be attained in a comparable natural system, and the authors believed that if the iron of the Clinton deposits was carried in true solution, then the limitations of the conditions under which this could occur were as they postulated.

The theoretical predictions of the behavior of iron in solution were based on the premise that iron solubility in natural waters is predictable within rather narrow limits if the pH and oxidation potential (Eh) of the environment are known. The experimental system covered a considerable range of pH, but was limited to a small range of Eh because the geologic occurrence indicated that the depositional basins were continuously saturated with oxygen under the partial pressure of the atmosphere.

The apparent good cross-checks among theory, experiment, and natural occurrence for the restricted conditions of the Clinton deposits led to a development of theoretical relations among the iron minerals over a greater range of Eh. It is possible to prepare diagrams showing the fields of stability of mineral hematite,[2] siderite, and pyrite as functions of pH and Eh for a sea-water system and to contour the solubility of iron on the diagram. Details of the calculations necessary can be found in Krumbein and Garrels (9, p 9); the resultant figure is shown here (Fig. 1). Slight modifications have been made in their original diagram; the present work led to small changes in some of the equilibrium constants used in the calculations.

James (7, 8) described several iron-mineral facies in the Precambrian deposits of the Iron River district of Michigan, and ascribed the differences in mineralogy to differences of environment. Although he did not actually discuss the occurrences in terms of a formal Eh-pH diagram, it is clear from his reconstruction of the environments that he assigns a major role to the oxidation potential. He recognized three chief iron-rich facies: a sulfide, a silicate, and

[1] Numbers in parentheses refer to Bibliography at end of paper.

[2] Since ferric hydroxide is precipitated and then loses water to form ferric oxide, the activity product of $Fe(OH)_3$ is used as the control for the formation of hematite. The water loss is variable; under some conditions hematite is formed, under others goethite. However, from the common occurrence of finely banded alternations of these two oxides, their solubility must be very similar.

a carbonate. He interprets all of these as primary sedimentary facies. In addition he describes a hematite facies in the Marquette district of Michigan that he also considers to be of primary origin.

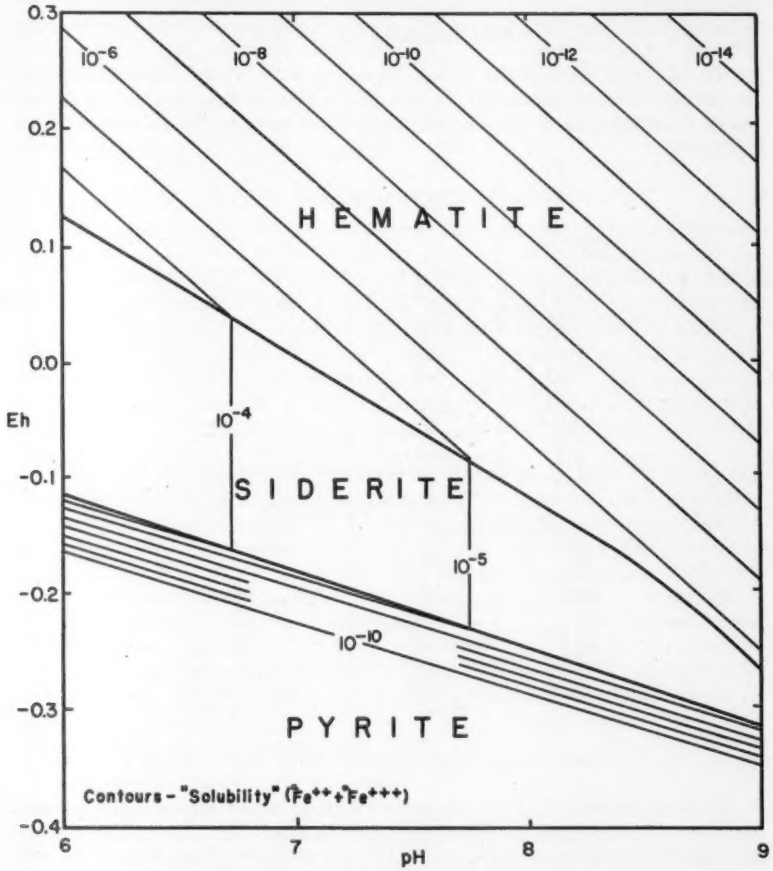


FIG. 1. Eh-pH stability fields for hematite, siderite, and pyrite in sea-water (after Krumbein and Garrels, 1952).

Thus, there exists a set of theoretical relations predicting distinct iron-mineral facies as functions of the depositional environment, and an independent recognition of such facies in the field (including a silicate facies for which chemical data are not available for theoretical treatment).

The purpose of this paper is to test the theoretical relations by experiments, and then to assess the three aspects—theoretical, experimental, and natural—in terms of their implications concerning the many problems of the origin of sedimentary iron formations.

THE EXPERIMENTAL SYSTEM.

In the earlier work on the Clinton type deposits, a "river" transporting iron was simulated by an aerated dilute ferrous chloride solution, and the "sea" into which it emptied by a sodium chloride solution in equilibrium with calcium carbonate.

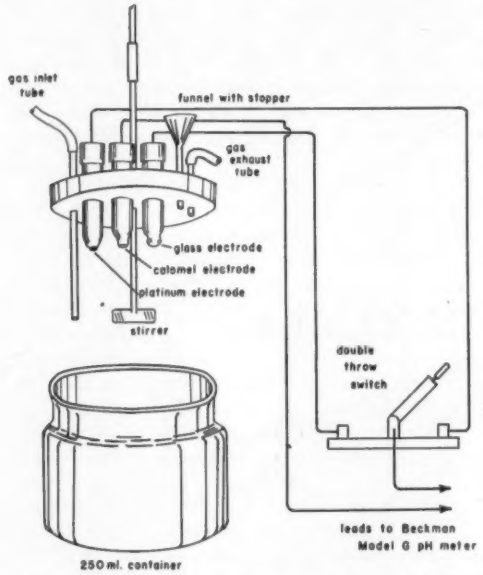


FIG. 2. Experimental apparatus for measurement of Eh and pH.

In the present work it was decided to start as before with a dilute ferrous chloride or mixed ferrous chloride-ferrous sulfate solution, but to subject it to a much greater variety of conditions—to remove dissolved air from it, to add carbon dioxide, to add calcium carbonate, to add sodium hydroxide, or to use various combinations of these treatments and reagents. Eh and pH were to be measured during the runs, and precipitates observed and identified if possible.

Experimental Apparatus.

The experimental apparatus is shown in Figure 2. A wide mouth glass jar of about 250 ml capacity was fitted with a rubber stopper. Through holes

in the stopper, three electrodes (platinum, glass, and saturated calomel) were inserted so as to project into the solution in the jar. These electrodes were connected to a Beckman Model G pH meter for direct determination of pH and oxidation-reduction potential (Eh), using the glass and saturated calomel electrodes for pH measurements, and the platinum and saturated calomel electrodes for Eh measurements. A double-throw switch was placed between the glass and platinum electrodes for convenient switching between pH and Eh readings.

Into other holes in the rubber stopper were inserted a stirrer, a tube for the introduction of various gases, a gas exhaust tube, and a stoppered funnel for the introduction of solids and liquids.

Experimental Procedure and Materials.

The ferrous chloride and ferrous sulfate used in the experimental runs were of reagent grade, the calcium carbonate was ground calcite of near-optical quality. Commercial bottled gases were sources of carbon dioxide and nitrogen. Nitrogen was used to sweep atmospheric gases from the solutions at various times during the experimental runs and was purified by bubbling through Fieser's solution (5, p 395). The CO_2 was not purified and may therefore have contained minor percentages of other gases. The gas exhaust tube on the apparatus was always open when gas was flowing, so the various gases in the experimental system were approximately at atmospheric pressure at all times.

The electrodes were checked against standard solutions before each run and the meter adjusted accordingly. They were again checked after each run to verify their proper operation during the runs. The pH meter was checked with a standard buffer solution for pH readings and with a standard redox solution described by ZoBell (14, p 495) for Eh determinations. The pH electrodes generally checked within $\pm$ 0.1 of a pH unit with a divergence of 0.2 of a pH unit on one of the longer runs. The Eh electrodes checked within $\pm$ 0.005 volts.

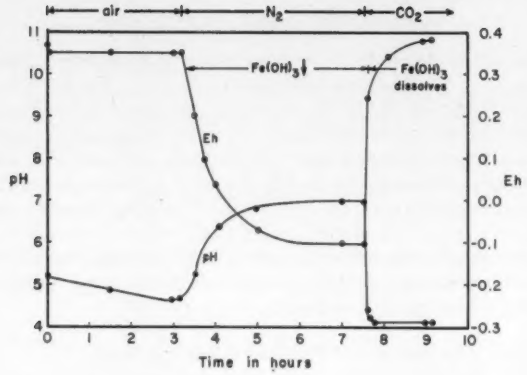
As standard Eh values are based on a zero value for the hydrogen half-cell, a further correction must be made for the saturated calomel electrode. The standard potential for the saturated calomel half-cell is given by ZoBell (14, p 495) at various temperatures:

Temperature	20° C	25° C	30° C
Potential in volts	0.249	0.246	0.242

This potential must be added to the actual observed potential (E) to obtain the Eh value for the system relative to the standard hydrogen electrode. As the experimental runs were carried out at room temperature, which varied from 22° C to 27° C, an average value of 0.246 was added to the observed values to obtain Eh values in the experimental system.

Experiments.

Run No. 1.—A 0.01 normal ferrous chloride solution was placed in the experimental apparatus. Air was bubbled through the solution until the pH



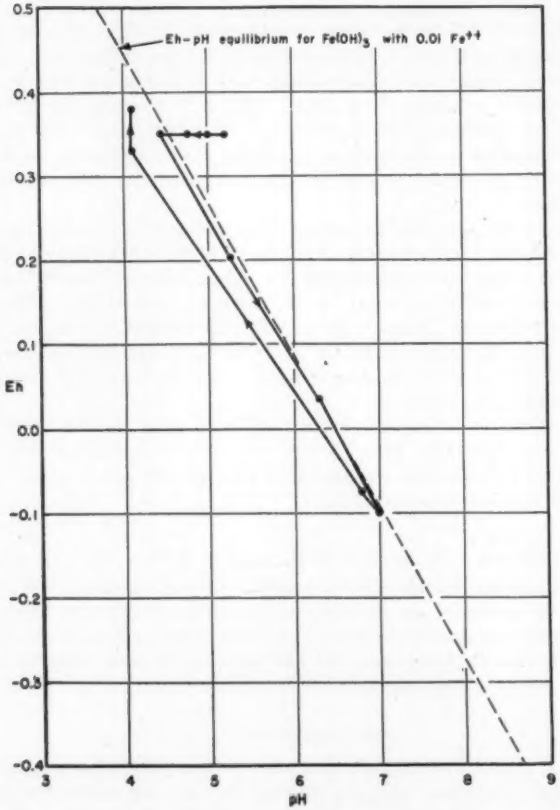


FIG. 3. Run No. 1—0.01 N $FeCl_2$. Eh and pH as functions of time.
FIG. 4. Run No. 1—Eh as function of pH.

and Eh of the system approached constant values. Nitrogen was then bubbled through the solution to remove the dissolved atmospheric oxygen and other gases. Finally, the system was saturated with carbon dioxide. No visible precipitate was formed during the run. The results are shown in Figures 3 and 4.

Run No. 2.—Run No. 2 (Figs. 5, 6) was also made with a 0.01 normal solution of ferrous chloride. Nitrogen was bubbled through the solution to remove the dissolved air, then solid $CaCO_3$, in the form of fine calcite (< 125 microns) was introduced into the system along with CO_2. The amount of calcite was not measured, but enough was added so as to have solid $CaCO_3$ in excess at all times.

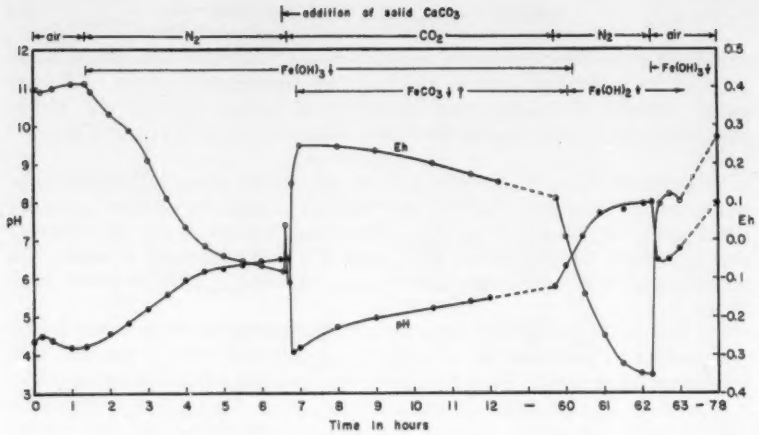
A light buff precipitate formed as a coating on the calcite grains. It was not possible to determine the composition of this buff colored material with the equipment at hand. Because it was precipitated as a thin coating on calcite grains, a test for carbonate ion was not practicable. Microscopic examination did not clarify the matter. However, from a consideration of the ions present in the system this material is probably $FeCO_3$ or possibly $Fe(OH)_3$. Then nitrogen was bubbled through the system, and a greenish-white precipitate of $Fe(OH)_2$ was formed.

Finally, air was bubbled through the system. Essentially all the remaining iron precipitated as ferric oxide. Upon standing in the presence of atmospheric oxygen, the $Fe(OH)_2$ previously formed was also oxidized to ferric hydroxide (oxide).

Run No. 3.—Run No. 3 (Figs. 7, 8) was made with a 0.1 normal ferrous chloride and 0.001 normal ferrous sulfate solution. When nitrogen was bubbled through the solution to remove the dissolved air the irregular nature of the rise of the pH curve and corresponding drop of the Eh curve is presumed to be due to the failure of the valve on the nitrogen tank to maintain a steady rate of flow. Solid calcium carbonate in the form of finely powdered calcite (< 125 microns) was added. Again, ferrous hydroxide came down as a greenish-white precipitate. The green ferrous hydroxide immediately oxidized to red-brown ferric hydroxide (oxide) upon filtration and exposure to the air.

Run No. 4.—Run No. 4 (Figs. 9, 10) was made with a 0.1 normal ferrous chloride solution. After bubbling nitrogen through the solution to remove the dissolved air, sodium hydroxide was added dropwise to the system to counteract the effect of the carbon dioxide and keep the pH up. Ferrous hydroxide precipitated when the pH approached 7. The presence of a slight amount of $FeCO_3$ in the precipitate was indicated by effervescence with hydrochloric acid.

Run No. 5.—Run No. 5 (Figs. 11, 12) was made with a 0.1 normal ferrous chloride and 0.001 normal ferrous sulfate solution. After the dissolved air was removed, CO_2 was bubbled through the solution. At a pH of 5.2 and an Eh of $+ 0.1$, a light buff colored precipitate began to form. This precipitate effervesced in normal hydrochloric acid and was therefore presumed to be siderite.



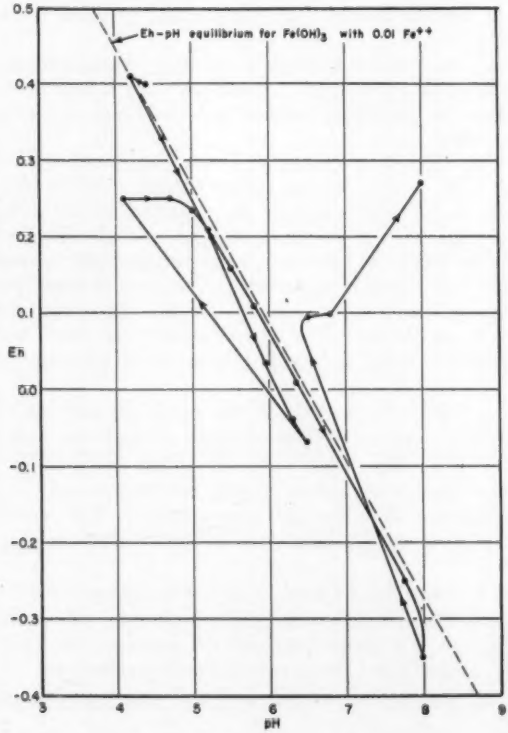
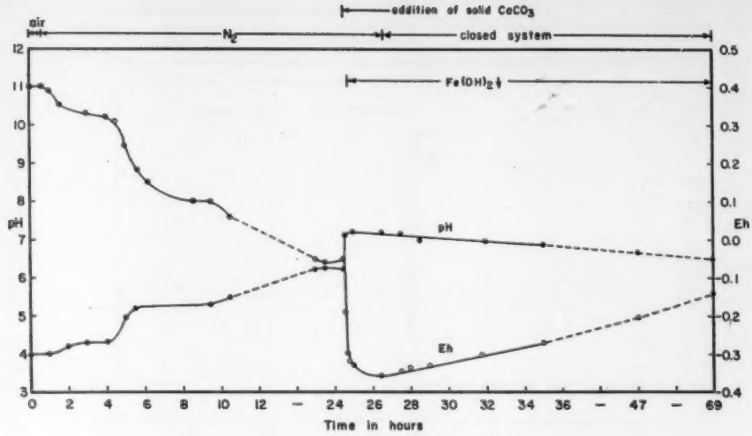


FIG. 5. Run No. 2—0.01 N $FeCl_2$. Eh and pH as functions of time.
FIG. 6. Run No. 2—Eh as function of pH.



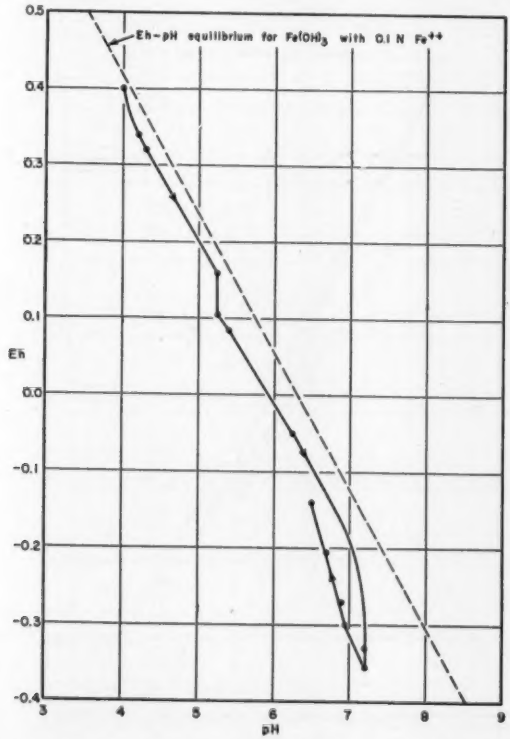
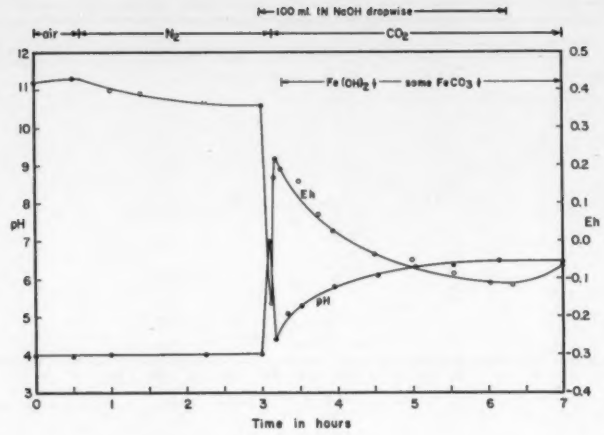


FIG. 7. Run No. 3—0.1 N $FeCl_2$ + 0.001 N $FeSO_4$. Eh and pH as functions of time.

FIG. 8. Run No. 3—Eh as function of pH.



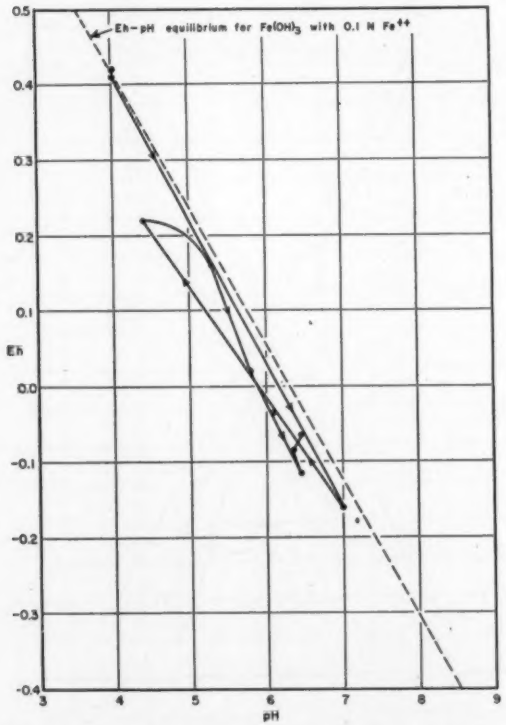
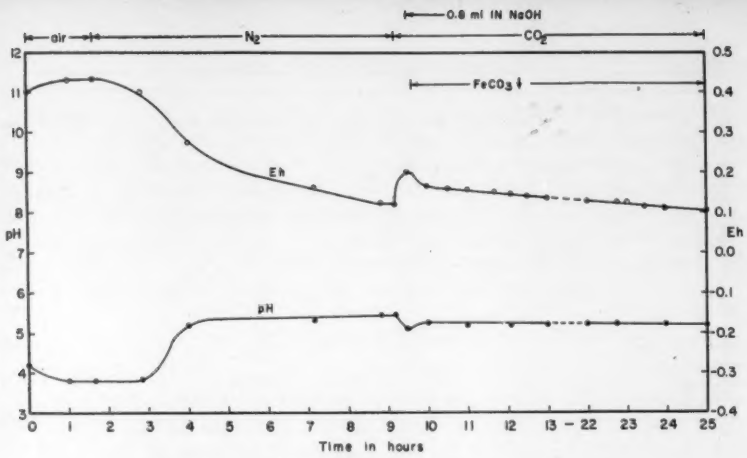
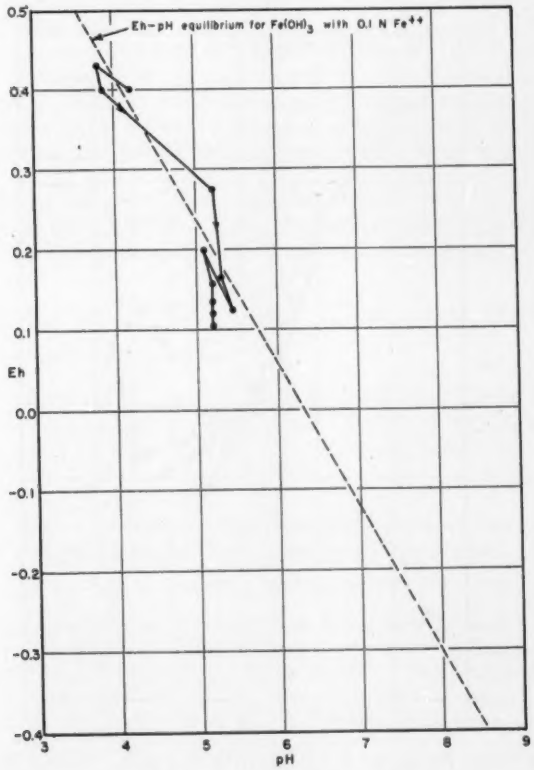


FIG. 9. Run No. 4—0.1 N $FeCl_2$. Eh and pH as functions of time.
FIG. 10. Run No. 4—Eh as function of pH.

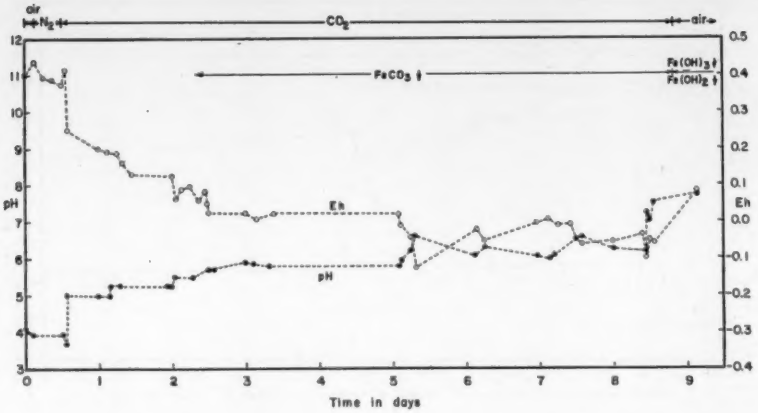




RUN No. 5 Eh as function of pH

FIG. 11. Run No. 5—0.1 N $FeCl_2$ + 0.001 N $FeSO_4$. Eh and pH as functions of time.

FIG. 12. Run No. 5—Eh as function of pH.



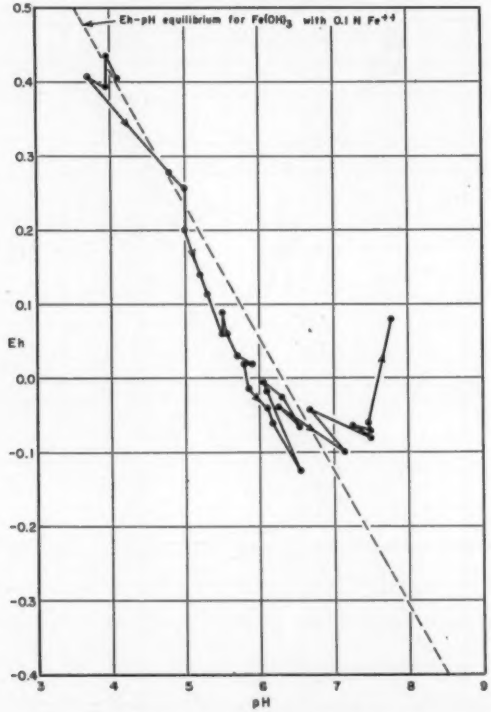


FIG. 13. Run No. 6—0.1 N $FeCl_2$ + 0.001 N $FeSO_4$. Eh and pH as functions of time.

FIG. 14. Run No. 6—Eh as function of pH.

Run No. 6.—Run No. 6 (Figs. 13, 14) was made with a 0.1 normal ferrous chloride and 0.001 normal ferrous sulfate solution. After removing the dissolved air, CO_2 was bubbled through the solution for nine days. During this time an appreciable quantity of fine, buff-colored precipitate formed which later effervesced when tested with hydrochloric acid. On the last day air was bubbled through the system. Iron precipitated as ferrous and ferric hydroxides. Tests upon the remaining solution with potassium ferrocyanide after filtration indicated that virtually all of the iron had been precipitated.

Discussion of Results.

All the runs show a general reciprocal relation between Eh and pH. The exceptions occur when air is admitted to a solution of high pH at the end of a run. The following explanation of the changes observed seems to fit the date.

Relation at Beginning of Runs.—The original ferrous chloride solution contains a little ferric ion. When it is first put into the reaction vessel it is very nearly in equilibrium with air, and only slight changes occur when air is bubbled through it. The original pH is generally between 4 and 5. This slight acidity can be attributed chiefly to atmospheric CO_2, with a small contribution from hydrolysis of the iron. Whatever the original ferric ion content of the solution, it appears that at the end of the period of bubbling with air the ferric ion is in equilibrium with ferric hydroxide, even though the solid phase is not visible.

For example, at the end of the air-bubbling stage in Run No. 1 (Fig. 3) the pH is 4.6 and the Eh is 0.35. From the fundamental Eh equation [3] it is possible to calculate the ratio of the activity of ferric to ferrous ion.

$$\mathrm{Eh} = \mathrm{E}^0 + \frac{RT}{nF} \ln \frac{a_{\mathrm{Fe}^{+++}}}{a_{\mathrm{Fe}^{++}}} \tag{1}$$

Under the experimental conditions:

$$0.35 = 0.771 + 0.06 \log \frac{a_{\mathrm{Fe}^{+++}}}{a_{\mathrm{Fe}^{++}}} \tag{2}$$

$$\frac{a_{\mathrm{Fe}^{+++}}}{a_{\mathrm{Fe}^{++}}} = 10^{-7} \tag{3}$$

Using the rough approximation that the activity of the ferrous ion ($a_{\mathrm{Fe}^{++}}$) is the same as its molarity in this dilute solution:

$$a_{\mathrm{Fe}^{+++}} = 10^{-7} \times 10^{-2.3} = 10^{-9.3} \tag{4}$$

At pH 4.6, the activity of H^+ is $10^{-4.6}$, and the activity of OH^- is $10^{-9.4}$ ($Kw = 10^{-14}$). If ferric ion is in equilibrium with ferric hydroxide, the activity product of ferric hydroxide should be equaled. The product is:

$$(a_{\mathrm{Fe}^{+++}})(a_{\mathrm{OH}^-})^3 = K_{\mathrm{Fe(OH)_3}}$$

$$(10^{-9.3})(10^{-9.4})^3 = 10^{-37.5}$$

[3] See Castano and Garrels, pp. 757 for sources of equation used.

Listed values of $K_{Fe(OH)_3}$ are $10^{-38.6}$ by Latimer (10) and $10^{-37.4}$ by Cooper (4), so that the calculated value checks reasonably well.

Effect of Nitrogen.—When air bubbling is followed by nitrogen, the pH increases, and the Eh decreases. The typical path is shown on Figure 3. The increase in pH takes place as atmospheric CO_2 is removed from the solution. As the pH increases OH^- ion increases, and the ferric ion concentration is reduced because of precipitation of $Fe(OH)_3$. The amount precipitated is infinitesimal, because the original concentration was only $10^{-9.3}$ molar (equation No. 4), but the decrease in ferric ion decreases the ferric-ferrous ratio, causing the corresponding decrease in measured Eh. The validity of this explanation, and the proof that equilibrium is maintained between ferric ion and the precipitated hydroxide, are shown in Figure 4.

The dashed line shows the theoretical pH-Eh relations if ferric ion is in equilibrium with the hydroxide; the experimental curve follows it very closely. The value for $K_{Fe(OH)_3}$ that is used is 10^{-38}—a compromise between Latimer's and Cooper's values. It is perhaps worth noting that the technique could be reversed, and activity products for hydroxides determined with considerable accuracy by using comparable experimental results, a straight line Eh-pH relation providing a measure of equilibrium.

Addition of CO_2.—When CO_2 is added after N_2 (Fig. 4), the solution becomes acid, and the small amount of ferric hydroxide precipitated redissolves. Again equilibrium seems to be attained quite rapidly. The changes in pH and Eh caused by nitrogen addition are retraced. The small deviation between the curves shows some time lag in the re-solution of the precipitated hydroxide, but the two converge in a matter of hours. This relation was not predicted—it was believed that the precipitated hydroxide would be recalcitrant. Unfortunately no aging experiments were run to see if equilibrium could be attained so rapidly after the hydroxide had opportunity to recrystallize. The implication is that colloidal ferric hydroxide (or oxide) responds rapidly to its environment, whether it is precipitated at the site of deposition or carried to it in colloidal dispersion.

When CO_2 alone is added to the solution, no precipitation of ferrous carbonate occurs, and none would be expected. Without the addition of some type of neutralizing agent, the distribution of the CO_2 is such that H_2CO_3 is by far the predominant species, and the $CO_3^=$ ion concentration is so vanishingly small that no ferrous carbonate could be formed. Precipitation of $FeCO_3$ would be expected when its activity product is exceeded:

$$a_{Fe^{++}} a_{CO_3^=} = 10^{-10.7} \qquad \text{(Latimer, 10, p 213)}$$

For the 0.01 normal (0.005 molar) Fe^{++} solutions used, precipitation should occur at carbonate ion activity of:

$$a_{CO_3^=} = \frac{10^{-10.7}}{10^{-2.3}} = 10^{-8.4}$$

In the experimental solutions saturated with CO_2, the pH at which this should

occur can be calculated from the H_2CO_3 equilibrium:

$$\frac{a^2_{H^+}a_{CO_3^{--}}}{a_{H_2CO_3}} = 10^{-17} \qquad \text{(Latimer, p 310)}$$

Under acid conditions $a_{H_2CO_3}$ is approximately equal to the solubility of CO_2 in water — 0.03 M. Solving for a_{H^+}:

$$a_{H^+} = \sqrt{\frac{10^{-17} \times 10^{-1.53}}{10^{-8.4}}} = 10^{-5.1}$$

or a pH of 5.1.

Presumably then, siderite will be formed if the CO_2 saturated solution is neutralized to a pH of 5.1 or higher. Addition of calcium carbonate to the solution raised the pH well above that value (Fig. 5), and a yellowish precipitate formed on the calcite grains. Presumably it was siderite, but no confirmatory tests could be devised with the equipment available. It was clear, however, that the amount of siderite formed was much less than the equilibrium quantity. When solid calcium carbonate alone was added without previous addition of excess CO_2 abundant ferrous hydroxide was precipitated at a pH of about 7, indicating that the release of carbonate ion from the calcium carbonate was not sufficient to form siderite. Rapid neutralization of a CO_2 saturated solution with NaOH (Run No. 4) precipitated both siderite and ferrous hydroxide, indicating again that the rate of precipitation of ferrous carbonate is so slow that it is easy to raise the hydroxyl concentration sufficiently to precipitate ferrous hydroxide metastably. In Run No. 5 only enough NaOH was added to raise the pH high enough to precipitate ferrous carbonate, but not high enough to precipitate ferrous hydroxide, and the precipitate was, as predicted, the carbonate. Also, precipitation was first observed at pH 5.3, as opposed to the theoretical value of 4.6 (for 0.1 NFe^{++} of Run No. 5) checking the theoretical relations fairly well.

In summary, ferrous carbonate precipitates under the predicted conditions, and equilibrium should be attained if precipitation were to take place over a period of a few weeks. The rate of reaction is low but appreciable. With rapid neutralization of the solutions ferrous hydroxide is precipitated metastably.

Precipitation of Ferrous Hydroxide.—Ferrous hydroxide was easily precipitated by simple neutralization of de-aerated ferrous chloride solution. If oxygen is removed, ferrous ion is not oxidized to ferric, and the lower valence hydroxide can be formed. The pH at which precipitation occurs is approximately that predicted by theory. Latimer (10, p 213) lists $10^{-14.8}$ as the activity product of $Fe(OH)_2$; for a 10^{-1} normal $FeCl_2$ solution the predicted precipitation pH would be 7.2; precipitation is observed at approximately that value. When the solution containing solid $Fe(OH)_2$ is exposed to air, the solid rapidly changes to reddish ferric hydroxide (oxide). Ferrous hydroxide is not listed as a mineral, but it does not seem impossible that it might occur, changing to the ferric compound before determination.

Attempts to Precipitate Ferrous Sulfide.—Ferrous sulfate in approximately the concentration of sea water was added to several of the solutions to see if

pyrite or other iron sulfide would be formed by reduction of sulfate under appropriate conditions. Even though the oxidation potential and the pH dropped well within the field where sulfate reduction would be expected (Run No. 2, at 62 hours), no iron sulfide was formed. This is fully to be expected; no examples of sulfate reduction in natural inorganic water solutions could be found

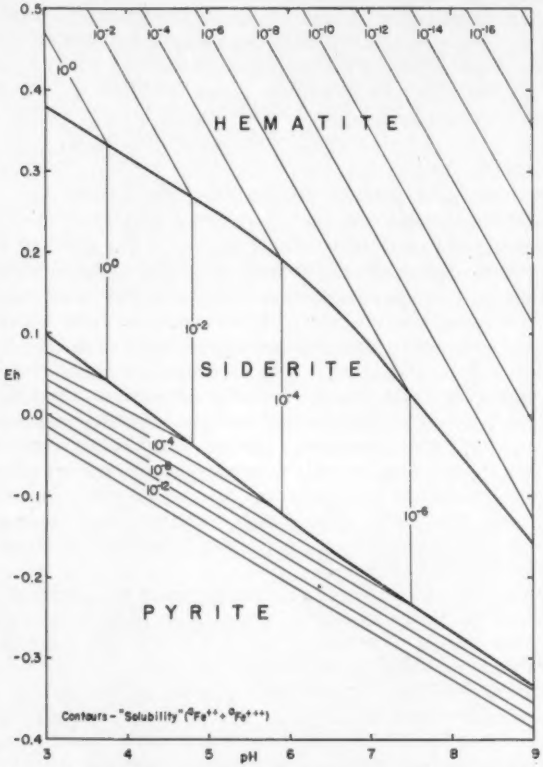


FIG. 15. Eh-pH stability fields for hematite, siderite, and pyrite in the experimental system ($SO''_4 = 0.0005$ M; $CO''_3 = 0.03$ M).

in the literature. The rate of the reaction is thus extremely slow; apparently it is catalyzed only by biochemical agencies such as bacteria.

Summary of Experimental Relations.—In the experimental system ferric hydroxide precipitated rapidly under the conditions predicted theoretically; equilibrium was maintained continuously. Ferrous carbonate also began to precipitate when its field was entered, but the rate of reaction was so slow that the experiments would have had to be carried out over a period of several weeks in order to reach equilibrium. It was possible, by rapid addition of reagents,

to precipitate ferrous hydroxide metastably within the siderite field. Sulfate ion was not reduced to sulfide.

The theoretical relations in the experimental system are summarized in Figures 15 and 16. Comparison of Figure 15 with Figure 1 shows that the field

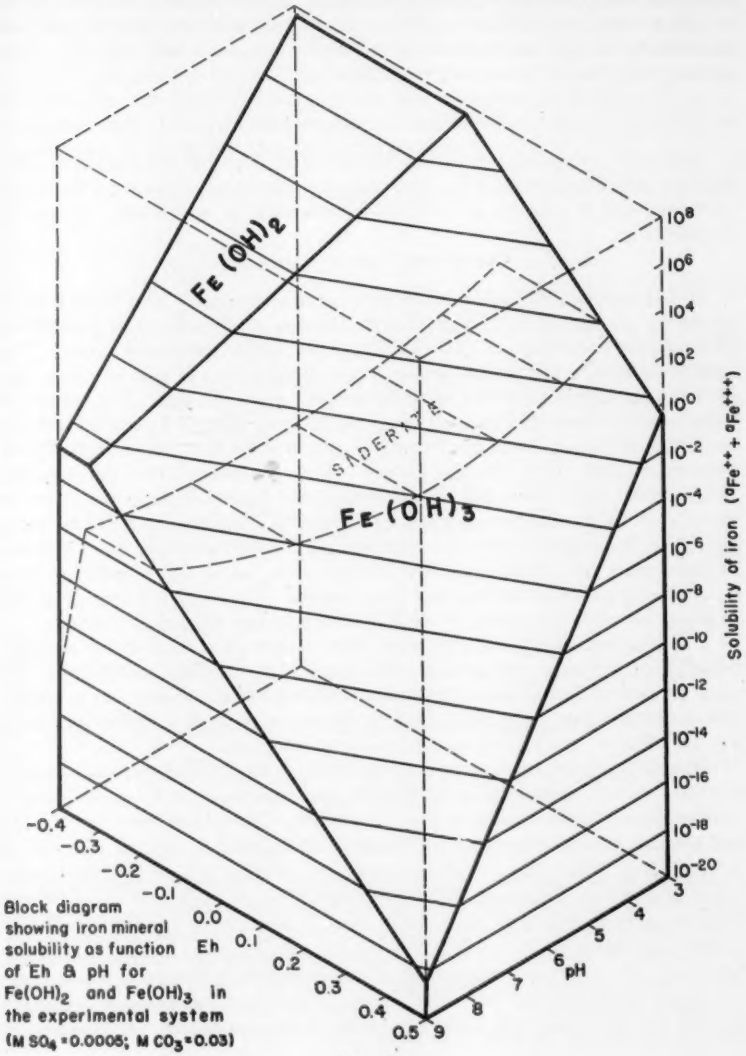


FIG. 16.

boundaries are not changed markedly by the differences between the experimental system and sea water. Figure 16 shows the relation of the metastable ferrous hydroxide to the stable compounds.

These diagrams are of course valid only for equilibrium for the chemical compounds under the stated conditions, but the little that is known of the effects of temperature and pressure on the equilibria used indicates that they are not significantly changed by temperature differences of 10 or 20 degrees, or by hydrostatic pressures of as much as 100 bars.

GEOLOGIC IMPLICATIONS.

The work, when considered in relation to the natural occurrence of sedimentary iron deposits, does not lead to any unequivocal answers to the major problems, but it perhaps narrows the framework in which they should be considered.

Source and Transport of Iron.

If it is assumed that most of the iron in the sedimentary iron formations is carried to the site of deposition in true solution in streams, it is possible to delineate the conditions of pH and Eh under which this could occur. The amount of iron in normal sea water is vanishingly low, so that any iron dissolved in streams is deposited when the streams reach the sea. The volume of water of some streams is so great, that even as little iron as 3 parts per million would be sufficient to form large iron-ore deposits if it could be deposited over a restricted area. For example, Gruner (6) has calculated that the Amazon, which carries but 3 parts per million iron, could form a deposit equivalent to the total of the Biwabik formation of Minnesota in 176,000 years. Three parts per million is a concentration of approximately 5×10^{-5} mols per liter; it seems to represent a reasonable minimum concentration below which sufficient iron is not carried to form a sedimentary iron deposit. Figure 17 has been prepared to show the conditions under which this minimum amount can be carried.

The diagram shows that this much iron cannot be carried under strongly reducing conditions at any natural pH. Under intermediate conditions of Eh it can be carried throughout the usual natural range of conditions, but as oxidation potentials rise, the acidity must be increased to hold a concentration of 5×10^{-5} M.

In well aerated natural waters the oxidation potential is of the order of 0.25 or 0.30. Under these conditions the pH would have to be between 5 and 6 to have the minimum amount of iron in solution. The pH of fresh water lakes and streams averages from 6.5 to 7.0 except in calcareous regions, in which it is from 7.5 to 8.4 (1, 11). Values between 5 and 6 are not exceptional; many rivers of northern Wisconsin have such characteristics. Thus it is not impossible to carry a little iron in solution even in well oxygenated rivers. Any oxygen deficiency, which would lower the Eh, would increase tremendously the amount of iron that could be carried. Oxygen-deficient streams are very common today because of human pollution of one type or another, but it is difficult to find data to show that such a condition exists naturally. Presumably a

slow-flowing stream with abundant organic material would be seriously oxygen-deficient in its bottom waters.

The optimum conditions for carrying iron in solution in rivers would occur in large sluggish streams containing abundant organic matter, draining areas of carbonate-free rocks. Such streams also would have small clastic loads, diminishing the problem of separating the solution load from the mechanical load. Perhaps one of the conditions that led to the extensive development of iron formations in the Precambrian was the availability of large drainage areas of carbonate-free rocks. However, this lack of carbonate surfaces is by no means proved. Dolomite was present in some of the areas marginal to the depositional basins in the Lake Superior Region.

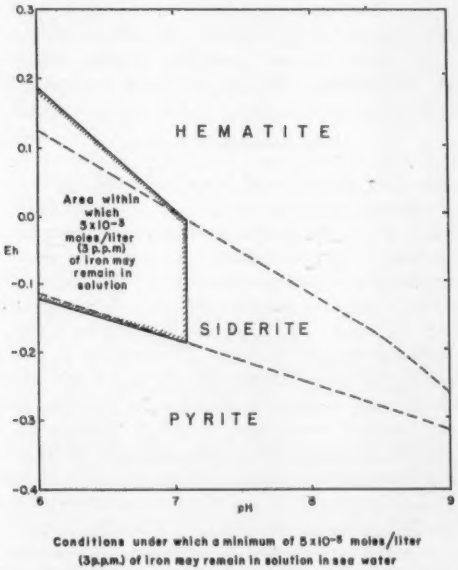


FIG. 17. Conditions under which a minimum of 5×10^{-5} moles/liter (3 ppm) of iron may remain in solution in sea water.

Separation of Iron from Clastics.

In addition to a medium capable of carrying sufficient iron in solution, a mechanism is neceessary to account for the great thicknesses of iron formation free from any significant quantity of clastic materials. It seems difficult to avoid the necessity for appropriate tectonic conditions, and the development of a clastic trap. Although it is no more than a suggestion, the appropriate conditions seem to develop as an intermediate stage between stable shelf conditions and formation of large continuously negative basins or troughs (8). The

Silurian Clinton ores (2) formed when a series of small basins were present; the stratigraphy of the Precambrian Marquette basin in Michigan is susceptible to such an interpretation. There, a sequence is found from clean quartzite to slate, to alternating slate-greywacke, to slate, to carbonate-silicate iron formation, to hematite iron formation. This could be interpreted as a change from shelf conditions (quartzite) to a deepening basin (slate-slate greywacke) to a stable basin (iron formation). The sequence from carbonate facies to hematite facies would represent very slow chemical filling of a deep stable basin, and the absence of clastics by the development of a second basin between the source and the basin of iron deposition, the second basin acting as a trap for the clastics. The area could be visualized as an unstable shelf, with a small basin developing, this becoming inactive as a second formed nearby. The stream would drain into the first basin, and the waters would have stream characteristics as they drained through a channel, or over a bar or sill to the second basin. There they would mix with marine waters, and iron precipitation would take place. Sakamoto (12) has described essentially this situation in his "paralic lakes."

Iron Mineral Relations.

The picture of a deep stable basin is well adapted for the interpretation of the gross mineral associations of the Iron River and Marquette areas of Michigan. At Iron River (7, 8), the iron-rich sequence changes from highly pyritic black slates at the base to ferrous silicate and carbonate above. At the Marquette area the sequence is from carbonate-silicate beds below to hematitic beds above. In the Iron River area one can picture a deep stagnant basin similar to those described by Strøm (13) off the Norwegian Coast, with stagnant waters rich in H_2S and organic matter. Presumably at this early stage the second or clastic-trapping basin has only begun to develop, and some fine clastics plus abundant colloidal organic debris have been carried into the basin and deposited with the chemical precipitates. As the trapping basin develops and becomes more effective, it stops more of the inorganic debris and organic material. The basin still is stagnant, but without abundant organic material the sulfate-reducing bacteria are not so active or abundant, and the iron minerals formed are the ferrous carbonate or silicate. The environment is oxygen deficient, but devoid of much active reducing material. Undoubtedly there is tectonic activity of the depositional basin, but the general picture seems to be one of filling; the hematite facies overlies the carbonate facies at Marquette, and apparently represents a shallower deposit because of the evidence of aeration. Aeration, of course, could be caused by other factors such as the development of convectional overturn, but the cutting off of the top of the hematitic beds by local unconformity also suggests shallowing water.

Sakamoto's (12) picture of the relation of the various iron minerals to seasonal changes in pH and oxidizing conditions corresponds rather closely with the views put forth at about the same time by Castaño and Garrels (3). Under oxidizing conditions, increase in pH forms precipitation of hematite, whereas decrease in pH favors precipitation of silica, giving a fundamental control for the alternating bands of the chert-hematite facies. Many factors

could give a rhythmic alternation of pH; the simplest perhaps would be a seasonal variation in river flow, causing a lowering of pH of the depositional basin when it is receiving large amounts of river water during floods, and an increase when stream volume drops and the effects of greater proportion of normal seawater are felt. Sakamoto (12) details the basis for such rhythmic changes without assuming any connection of the depositional basin with the sea. A rhythmic seasonal change in pH has been measured in the English Channel (4) although this change is not directly related to stream flow. The important point is that rhythmic pH changes can be produced by a variety of mechanisms. The superimposition of such changes on changing oxidation potential values gives a rational basis for the mineral associations found in iron-rich rocks. Pyritic slates represent strongly reducing conditions in a stagnant basin receiving some fine-grained clastics and abundant organic debris; siderite-chert alternations reflect rhythmic fluctuations of pH in a deoxygenated basin with little organic material and essentially no inorganic clastics. With increasing pH the carbonate precipitates, with decreasing pH, the silica. The chert-hematite association is the oxygenated equivalent, with the iron oxide forming during the increasing pH stage.

The relation of the iron silicates to the other minerals is still not clear. So little is known about the distribution of silicate ion species as functions of pH, and conversely of the relation of precipitated silicates to the kinds of silicate ions in solution, that no suggestions seem appropriate.

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NOTES ON THE DIFFERENTIAL LEACHING OF URANIUM, RADIUM, AND LEAD FROM PITCHBLENDE IN H_2SO_4 SOLUTIONS.[1]

GEORGE PHAIR AND HARRY LEVINE.

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ABSTRACT.

Two 5-pound samples from the "hot spot" of the pyritic dump of the Wood mine, a past producer of pitchblende near Central City, Colo., showed Ra/U ratios that were abnormally high but nearly constant at about 150 times the equilibrium value for both samples in spite of a sevenfold difference in uranium contents. Analyses of oxidized but still black pitchblende from Katanga, in the Belgian Congo, before and after leaching in very dilute, dilute, and concentrated sulfuric acid solutions showed that: (1) UO_3 is preferentially leached with respect to UO_2, Ra, and Pb in all three solutions, (2) the resulting residual concentration of both radium and lead effected in the process is proportional to the total amount of uranium leached except in concentrated H_2SO_4, and (3) after a sample has been leached in concentrated H_2SO_4 the resulting increase in radium content relative to lead is much lower, as might be expected from data published by Lind, Underwood, and Whittemore in 1918 for the solubility of $RaSO_4$. Under similar leaching conditions, unaltered pitchblende from Great Bear Lake, in Northwest Territory, Canada, lost only 1/10 to 1/15 as much uranium as the UO_3-rich Katanga ore. Both laboratory and field results point to the same conclusion: in an oxidizing, highly acid environment uranium is rapidly leached and both radium and lead tend to be fixed about proportionally in the process. These results help to explain (1) why UO_3-rich uranium minerals tend to give maximal Pb/U ages and (2) why the search for high-grade uranium ore in and around abandoned sulfide mines known to have produced pitchblende in the past has been consistently disappointing.

INTRODUCTION.

THE complex solutions involved in the leaching of pitchblende in pyritic mines and dumps are characterized by their relatively high contents of free H_2SO_4.

[1] Publication authorized by the Director, U. S. Geological Survey.

For example, water from the Idaho Tunnel, 5 miles from Central City, Colo., has been found to contain 0.13 g per liter of hydrogen ion and 18,260 ppm of $SO^{=}_{4}$ ion (3).[2] It is, therefore, a 0.13 N solution of H_2SO_4. Bastin and Hill (1), in describing the pyrite-rich iron mine in Russel Gulch near Central City, state, "The waters of this mine are so corrosive that the overalls of miners working in wet places are sometimes eaten to shreds in a day or two, and iron rails, pipes and nails must be frequently replaced." Pitchblende was recently discovered in a newly opened stope in this mine, but none has been found on the leached walls of the older workings.

The results of the redistribution of uranium and radium brought about by such solutions have been recognized by field geologists for some time, but little attention has been given to the processes involved. This paper presents quantitative field and laboratory data on the results of sulfuric acid leaching of certain pitchblende ores. The conclusions are believed to have a direct application to the problem of finding uranium in areas of sulfide deposition and to the problem of age determinations by lead-uranium and lead-lead methods.

This study is part of the U. S. Geological Survey's program of uranium reconnaissance in the Colorado Front Range sponsored by the U. S. Atomic Energy Commission. It is one phase of the writers' continuing study of the geochemical cycle of uranium deposition in the Central City district. Data on the distribution of uranium in the radioactive porphyries and hydrothermal veins of this district have been summarized in another report (11). Some aspects of the distribution of uranium in the pre-Cambrian rocks in the Central City district are now being investigated.

F. S. Grimaldi, of the Geological Survey, supplied much useful information on chemical matters in the course of this work. J. Bracken and R. Champion, also of the Geological Survey, made the radium determinations by the radon method, without which these studies would not have been possible.

FIELD SAMPLING.

The radium-rich dump material of the Wood mine, located in the pitchblend belt near Central City, Colo., provided an excellent starting point for studies of the fractionation of radium with respect to uranium in nature. This long-abandoned mine still retains second rank among the Nation's mines in total production of pitchblende. More than 150 tons of crude ore, mostly high grade, was mined between 1872 and 1917. During the field season of 1949 R. U. King, of the U. S. Geological Survey, pointed out to one of the authors an extremely radioactive "hot spot" on the weathered dump. From a distance of 18 inches the "hot spot" gave a maximum reading of 12 mR/hr on the 20 mR/hr scale of a beta-gamma survey meter.

The present owners of the Wood mine attempted, by wet tabling methods, to recover the radioactive constituent, believed to be pitchblende, from several truckloads of heterogeneous dump material, but their attempts were unsuccess-

[2] Numbers in parentheses refer to Bibliography at end of paper.

ful. The writers then obtained negative results on uranium flux tests of radioactive samples from this mine, and these results were confirmed by uranium analyses of radioactive samples collected by Charles Towle, of the Atomic Energy Commission, and R. U. King. The foregoing tests indicated that the very high radioactivity of the dump material was due either to the presence of daughter products of uranium or to the presence of a member of the thorium series.

To provide material for mineralogic and chemical study, two 5-lb samples of the heterogeneous dump material from the Wood mine were collected—one, P4a, from the surface at the center of the "hot spot"; the other, P5a, 18 inches directly below the first. Together these samples made up at least 10 percent of the material in the "hot spot."

STUDIES OF DUMP SAMPLES.

The recognizable fragments in these two 5-lb samples consisted chiefly of more or less decomposed granite wall rock together with a little quartz-rich vein material leached of its pyrite. Most of both 5-lb samples consisted of weathered "clay" or "gouge" produced by the decomposition of both wall rock and vein material. Semiquantitative spectrographic analyses on splits of the crushed samples showed only the constituents typical of granite with, at most, a very small percentage of metallic elements, including iron, copper, zinc and lead.

The "clay" was highly radioactive. No uranium minerals were observed under the binocular microscope, but a small amount of fine-grained pitchblende was extracted from both samples in methylene iodide. The chief metal minerals present in the heavy mineral fractions, in order of decreasing abundance, were chalcopyrite, pyrite, and sphalerite.

To minimize segregation, both bulk samples were split with a Jones splitter, crushed to 60 mesh, mixed, and again split. All analyses—spectrographic, chemical, and radiometric—were made on the same splits. The equivalent uranium contents determined by laboratory beta-gamma counts averaged about 85 times the amount of uranium determined chemically. A vertical chamber and an end-window counter were used in these measurements; the results are low, if anything, owing to the loss of radon by emanation. The same samples were analyzed for thorium by the nephelometric method (6), for uranium by the fluorimetric method (7), and for radium by the radon method (4).

The results of these analyses (Table 1) show that:

1. The high radioactivity of both samples is caused largely by concentrations of radium. To satisfy the radium-uranium equilibrium, a uranium content of 13 percent would be required in sample P4a, whereas it contains only 0.085 percent uranium. Thoria was negligible (0.002 by weight percent in both samples).

2. Both samples have radium-uranium ratios that are abnormally high but nearly constant in spite of a sevenfold difference in uranium content. The radium-uranium ratios average 150 times their equilibrium value.

This high but nearly constant radium-uranium ratio suggests that more than 99 percent of the uranium originally present in the "hot spot" of the dump had been leached, leaving the "hot spot's" radium content fixed in situ. Such high concentrations of short-lived radium could have been formed only very recently, probably since the high-grade uranium ore was thrown out on the dump. It seems difficult, if not impossible, to conceive of any process that would introduce radium in a constant ratio to the amount of uranium originally present, or that would introduce both radium and uranium in fixed proportions exceeding their equilibrium ratio by 150-fold.

As both samples were closely associated one above the other on the dump, it seems logical to assume that both steeped in the same supergene solutions, and as a result the leaching of uranium from each sample was proportional to the amount originally present. The simultaneous fixing of the radium content is to be expected in view of the extreme insolubility of $RaSO_4$ in dilute acids containing the common ion $SO^{=}_4$. The experimental results described confirm

TABLE 1.

RESULTS OF ANALYSES OF DUMP MATERIAL FROM THE "HOT SPOT" OF THE WOOD MINE.

Sample	Radium (Weight percent)	Percent uranium in equilibrium with Ra (calculated)	Actual uranium in samples (percent)	Percent of original U leached	Ra/U (meas.)	Radium enrichment factor
P4a	4.46×10^{-6}	13.1	0.085	99.3	52.5×10^{-6}	154
P5a	5.53×10^{-7}	1.62	0.011	99.3	50.3×10^{-6}	148

the residual concentration of both radium and lead and show that the amount of such concentration is about proportional to the amount of uranium leached in dilute H_2SO_4 solutions.

These particular quantitative results of the field sampling apply only to the material in the "hot spot" of the dump. Considerable lateral variation across the dump is anticipated in view of the large differences in amount and composition of the leaching solutions formed at widely separated points. The process, however, probably operates throughout the dump area, and the differences are ones of degree of leaching.

LABORATORY LEACHING STUDIES.

Available data on which to base a prediction as to the relative solubilities of mechanical mixtures of UO_2 and UO_3 in H_2SO_4 include, for example, the fact that UO_3 forms uranyl salts in acid solution according to the relation

$$UO_3 + H_2SO_4 \rightleftharpoons UO_2^{++} + SO_4^{=} + H_2O$$

and that these uranyl salts are very soluble in aqueous solutions. On the other hand, UO_2 is relatively insoluble in nonoxidizing acids, including HF, and in their aqueous solutions.

The mixtures of UO_2 and UO_3 in the variable mineral pitchblende, however, are not mechanical mixtures but show the predominant face-centered cubic structure of UO_2, in spite of the presence of a minimum of 15 percent UO_3, which is generally interpreted as the result of auto-oxidation. Supergene oxidation of pitchblende results in greatly increased U^{+6}/U ratios with corresponding decrease in specific gravity and hardness, but a relict uraninite structure is retained until an advanced stage. The UO_3 formed is apparently amorphous to X-rays.

According to Brooker and Nuffield (2), "Specimens [of pitchblende] relatively low in U^6 gave sharp X-ray power photographs. With increasing U^6/U, back reflections became weak and diffuse, then low-angle reflections became diffuse, and finally with $U^6/U = 85.0\%$ no pattern was obtained. The corresponding cell edges decreased from 5.45 kx for $U^6/U = 17.4\%$, as compared to 5.46 for synthetic UO_2, to 5.39 for $U^6/U = 78.5\%$. Therefore, in the 6 specimens the quality of the X-ray pattern and the cell sizes are related to the degree of oxidation."

In view of the predominance of the UO_2 structure it seems logical that the UO_3 in the pitchblende would be less readily available for leaching than the same amount in a comparable mechanical mixture. Accordingly a series of experiments was designed to test the relative leachability of the various components of pitchblende in H_2SO_4 solutions. Like the pitchblende found on the dumps and exposed on the walls of the abandoned mines, the material selected had undergone partial supergene oxidation.

Pitchblende ore from Katanga was hand-picked to provide 10 g of high-grade concentrate containing 67.31 percent uranium. This concentrate consisted of nearly pure pitchblende with less than an estimated 2 percent of not easily removable yellow secondary uranium minerals. Analysis showed that, although the pitchblende was black, it contained more UO_3 than UO_2. The 10-g sample was ground fine in a mortar and five 2-g splits were taken. Two of the 5 splits were reserved for future work.

One of the splits was leached in concentrated H_2SO_4, one in 1.84 N H_2SO_4, and one in 0.17 N H_2SO_4. Over a three-day period a total of 31 ml of acid (at room temperature) was used for each. The solutions were shaken for a few minutes daily, but otherwise no attempt was made to keep them stirred. Each sample was leached for 144 hours. At the end of 24, 48, and 72 hours, 2 ml of each solution was removed for U analysis; an equal quantity of fresh acid was added after each removal to keep the volume constant at 25 ml. All solutions were analyzed for uranium after 144 hours.

The results are somewhat variable, but they indicate that in the more concentrated solutions almost all the soluble uranium went into solution within 24 hours and that thereafter the uranium content of the solution remained fairly constant. Only in the dilute (0.17 N) solutions does the uranium content of the solution show a steady increase with time. The data are given in Table 2.

The leached samples were filtered at the end of 144 hours; the filtrate from the concentrated H_2SO_4 was washed with about 30 ml of distilled water. The

wash water was found to contain almost as much uranium (0.013 g/ml) as was in the concentrated acid, which fact suggests the formation of a uranium sulfate relatively insoluble in concentrated H_2SO_4 but soluble in H_2O. Because of this loss of uranium in washing, the results of the uranium analyses of the concentrated H_2SO_4 solutions cannot be used to compute the actual amount of uranium leached from the 2-g sample. The results on the filtrates from the other two solutions are satisfactory and permit such computations to be made (Table 3).

The leached and unleached splits were analyzed for U, UO_2, UO_3, PbO, and Ra with the results shown in Table 4. The method of Hillebrand and Lundell (8) was used in the UO_2 analyses. The unleached sample was found to contain only 0.013 percent by weight ThO_2. The selective leaching of UO_3 from the pitchblende in all three concentrations of H_2SO_4 is clearly shown in Table 5.

Effect of the H_2SO_4 Leach on the UO_2/UO_3 Ratio.—If all the uranium leached were in the form of UO_3, the resulting UO_2/UO_3 ratio would be higher. We infer that some UO_2 was also leached in the process, but the amount was relatively small compared with the change in UO_3.

TABLE 2.

URANIUM CONTENT OF H_2SO_4 SOLUTIONS OF PITCHBLENDE, IN G/ML.

Time (hours)	Conc. H_2SO_4		1.84 N H_2SO_4		0.17 N H_2SO_4	
	Katanga	Great Bear L.	Katanga	Great Bear L.	Katanga	Great Bear L.
24	0.013	0.0006	0.020	0.0027 (?)	0.008	0.0014
48	0.013	0.0006	0.022	0.0008	0.010	0.0004
72	0.013	0.0007	0.034 (?)	0.0013	0.012	0.0006
144	0.014	0.0006	0.016	0.0012	0.014	0.0004

Effect of the H_2SO_4 Leach on the Pb/U Ratio.—Because of the relative insolubility of lead compared with UO_3 in H_2SO_4 solutions, the pitchblende shows an increase in lead content after leaching in all three solutions. The amount of this increase is roughly proportional to the amount of uranium leached, indicating that the greater part of the lead contained in the soluble uranium is fixed, probably as the sulfate. The resulting increase in the Pb/U ratio was sufficient to change uncorrected apparent ages from approximately 760 million years to as much as 1,100 million years.

Except in the concentrated H_2SO_4 the relative increase in the Ra/U ratio after leaching is similar to the relative increase in the Pb/U ratio. The large difference between the relative Pb/U ratio and the relative Ra/U ratio after leaching in concentrated H_2SO_4 (Table 5) probably results from the greatly increased solubility of $RaSO_4$ in concentrated H_2SO_4. According to Ellsworth (5) ". . . though the presence of 50 percent sulfuric acid has no appreciable effect on the solubility [of $RaSO_4$] at higher acid concentrations the

TABLE 3.

AMOUNT OF URANIUM LEACHED FROM 2-G SAMPLES OF PITCHBLENDE

1.84 N H_2SO_4			0.17 N H_2SO_4		
ml	U content (g/ml)	Total	ml	U content (g/ml)	Total
Katanga					
2	× 0.020	= 0.040	2	× 0.008	= 0.016
2	× 0.022	= 0.044	2	× 0.010	= 0.020
2	× 0.034	= 0.068	2	× 0.012	= 0.024
25	× 0.016	= 0.400	25	× 0.014	= 0.350
Total U leached		= 0.552 g/2-g sample	Total U leached		= 0.410 g/2-g sample
		or 0.276 g/g sample			or 0.205 g/g sample
Percent of original U leached:		41.00	Percent of original U leached:		30.46
Great Bear Lake					
2	× 0.0027	= 0.0054	2	× 0.0014	= 0.0028
2	× 0.0008	= 0.0016	2	× 0.0004	= 0.0008
2	× 0.0013	= 0.0026	2	× 0.0006	= 0.0012
25	× 0.0012	= 0.0300	25	× 0.0004	= 0.0100
Total U leached		= 0.0396 g/2-g sample	Total U leached		= 0.0148 g/2-g sample
		or 0.0198 g/g sample			or 0.0074 g/g sample
Percent of original U leached:		4.66	Percent of original U leached:		1.74

solubility increases rapidly." The relative increase in solubility of $PbSO_4$ in concentrated H_2SO_4 is much less than the change in solubility of $RaSO_4$. Lind, Underwood, and Whittemore (10, p 465) measured by the emanation method

TABLE 4.

ANALYSIS OF LEACHED AND UNLEACHED SPLITS.

	U	Percent by weight			Ra (curies/g)
		UO_3	UO_2	PbO	
Unleached	67.31	33.19	45.72	7.68	1.96×10^{-7}
Leached:					
Conc. H_2SO_4	63.9	46.48	27.60	10.86	1.99×10^{-7}
1.84 N H_2SO_4	68.16	45.06	28.46	10.19	2.67×10^{-7}
0.17 N H_2SO_4	68.58	41.64	38.30	9.51	2.37×10^{-7}

TABLE 5.

RATIOS OF UO_3/UO_2, Pb/U, AND Ra/U.

	UO_3/UO_2	$\frac{UO_3/UO_2 \text{ (leached)} \times 100}{UO_3/UO_2 \text{ (unleached)}}$	Relative Pb/U ratio	Relative Ra/U ratio	$Ra/U \times 10^{-7}$ (meas.)
Unleached	0.727	—	1	1	2.91
Leached:					
Conc. H_2SO_4	1.68	231	1.48	1.07	3.114
1.84 N H_2SO_4	1.61	221	1.30	1.34	3.917
0.17 N H_2SO_4	1.25	171	1.21	1.18	3.455

an extremely rapid increase in solubility of $RaSO_4$ with increase in concentration of H_2SO_4 above 65 percent. The solubilities listed in Table 6 are taken from their data. The differential leaching of uranium with respect to lead from our partly oxidized pitchblende is shown in Table 7. Apparent ages were interpolated from Wickman's graphs (12).

Effect of the H_2SO_4 Leach on the Ra/U Ratio.—The average Ra/U ratio in the unleached oxidized pitchblende was slightly low, 2.91×10^{-7} g Ra/g U

TABLE 6.

SOLUBILITY OF $RaSO_4$ AT 23° C.

	Grams per 25-ml solution
0.10 N H_2SO_4	2.2×10^{-4}
1.0 N H_2SO_4	2.2×10^{-4}
10.0 percent H_2SO_4	2.4×10^{-4}
60 percent H_2SO_4	6.3×10^{-4}
65 percent H_2SO_4	6.4×10^{-4}
*70 percent H_2SO_4	$> 79.0 \times 10^{-4}$

* Solution not saturated.

as compared with 3.4×10^{-7} g Ra/g U at equilibrium, the figure generally accepted at present for unaltered uranium minerals (5). A definite increase in the Ra/U ratio took place after the pitchblende was leached in all three H_2SO_4 solutions. The apparent increase in radium content of the two samples leached in dilute solutions is roughly proportional to the amount of uranium leached. The increase in the Ra/U ratio is given in Table 5.

TABLE 7.

DIFFERENTIAL LEACHING OF U WITH RESPECT TO Pb.

	U leached (g/g sample)	Calc. Pb in U leached (g/g sample)	Apparent increase in Pb (g/g sample)	Pb/U ratio	Uncorrected apparent age (million years)
Unleached				0.106	760
Leached:					
Conc. H_2SO_4				0.157	1,100
1.84 N H_2SO_4	0.275	0.029	0.023	0.138	975
0.17 N H_2SO_4	0.205	0.022	0.017	0.129	910

APPLICATIONS TO THE PROBLEM OF AGE DETERMINATION

These experiments are believed to have a direct application to the problem of apparent age determinations by lead-uranium and lead-lead methods. The leaching by natural H_2SO_4 solutions of uranium minerals rich in UO_3 as compared with UO_2 may be expected to lead to an enrichment both in total lead and in radium relative to uranium. Where considerable importance is to be attached to age determinations on a few samples, and where a high degree of accuracy in the final results is desired, not only should the samples be collected with special care, but their geological environment should be fully described. So-called sooty pitchblende—the soft, earthy variety having very low specific gravity—seems particularly susceptible to solution in H_2SO_4, and for the present, apparent ages based on such material should be regarded with some skepticism, particularly when based on single samples. These conclusions agree with the generalization of Ellsworth (5), to the effect that uranium minerals with very high UO_3/UO_2 ratios, including altered uraninites and most secondary uranium minerals, tend to have misleadingly high Pb/U ratios.

The total lead extracted from uranium minerals differs from "normal common lead" in that it contains relatively greater proportions of the uranium daughters, Pb^{206} and Pb^{207}, as compared with the nonradiogenic Pb^{204}. For the present discussion the thorium-lead, Pb^{208}, may be neglected. To obtain corrected lead-uranium and lead-lead ratios, Pb^{204} is generally used as the common lead index and appropriate amounts of Pb^{206} and Pb^{207} are deducted from the total lead in the proportion in which these isotopes are found in so-called common lead. The excess Pb^{206} and Pb^{207} represent the contribution of the U^{238} and U^{235} originally present in the sample. It follows that, where uranium has been leached, the corrected amounts of Pb^{206} and Pb^{207} will be too high, and, depending on the extent of the leaching, apparent ages based on the Pb^{206}/U^{238} and Pb^{207}/U^{235} ratios will be increased accordingly. In general, the effect on the Pb^{207}/U^{235} age will be greater than that on the Pb^{206}/U^{238} age, but both will be increased. The relative change in a Tertiary apparent age is of course much greater than that in a Precambrian for the same amount of leaching.

Recent leaching (being a chemical process) has little effect on the Pb^{207}/Pb^{206} ratios. When, however, such leaching has been active over a considerable interval of geologic time, the residual concentration of short-lived radium could lead to increased corrected ratios of Pb^{206} relative to Pb^{207}, resulting in impossibly young Pb^{207}/Pb^{206} apparent ages. Unfortunately lead-lead ages are so sensitive to experimental error and to the composition of the common lead used in the correction that they are of little value in age determinations on minerals younger than 200 million years, as shown by Holmes (9, p 140). As a result, in dealing with geologically young minerals, impossibly young ages are usually attributed to experimental error in the isotopic analyses. Our data are scanty and based on impure material, but they are adequate to show that unaltered pitchblende having the normal large excess of UO_2 over UO_3 is much less readily attacked by sulfuric acid solutions, and from this point of view it can be expected

to yield more reasonable apparent ages. We hand-picked the laboratory collection of ore from Great Bear Lake and obtained 20 grams from alteration products. It contained a high percentage of metallic impurities, chiefly cobalt-nickel arsenides, and as a result had a low total uranium content (42.46 percent). The arsenic probably had a reducing effect during the analysis on any UO_3 present because nearly all the uranium was found to be in the quadrivalent state. In view of their unreliability, the figures for UO_2 are not given. The results of the leaching of a 2-g sample in sulfuric acid solutions are given in Table 2. Again there is no systematic increase in uranium content of the solutions with respect to time.

Calculations show that the percentage of the original uranium leached from the UO_3-rich Katanga sample is 10 to 15 times that leached from the pitchblende from Great Bear Lake in similar solutions (Tables 2, 3). It is apparent that figures for the "solubility" of pitchblende have little meaning unless the UO_2/UO_3 ratio is specified at least approximately.

APPLICATIONS TO URANIUM SURVEYS IN MINERALIZED AREAS.

The results of these investigations show clearly that unaltered pitchblende is itself relatively insoluble in even the most concentrated solutions of H_2SO_4 at room temperatures. Once, however, it has become partly oxidized by contact with oxygen, either in the air or dissolved in the mine waters, the pitchblende is readily susceptible to solution by the H_2SO_4 invariably present in and around sulfide mines. Mine waters containing at least as much H_2SO_4 as the 0.17 N solution used in some of these experiments are inferred to be common in the pyritic mines of the Central City district. Although the pitchblende remaining on the walls of the mine workings is on the whole less readily permeated by the solutions than were the pulps used in these experiments, ample time has been available for the leaching (20 to 50 years). The leaching on the scale indicated by the analyses of the dump material and demonstrated in the laboratory helps to explain several present-day peculiarities in the distribution of uranium in the Central City district, including:

1. The scarcity of pitchblende and of secondary uranium minerals on the dumps of the chief pitchblende producers.

2. The nearly complete absence of pitchblende and of secondary uranium minerals from the surface outcrops of mineralized veins known to carry pitchblende at depth.

3. The apparent absence of pitchblende from the oxidized zone. Very little pitchblende has been found within 100 feet of the present surface although the records show that the two largest uranium producers—the Kirk and Wood mines—have levels at 50 and 97 feet, respectively, which were worked for gold.

4. The scarcity of pitchblende and uranium minerals in the abandoned dewatered mines that are known to have produced pitchblende in the past. The evaluation of the uranium potential of such mines by radiometric surveys and by shallow channel sampling has been consistently discouraging. Important new discoveries throughout the Front Range have generally been the result of relatively recent stoping.

In a highly acid, oxidizing environment it is apparent that a small amount of pitchblende remaining on the surface of the leached mine walls may indicate considerably larger amounts at greater depth in the walls. Only by deep channel sampling or by drilling could the uranium reserves of such a mine be properly assessed. Local high concentrations of radium relative to uranium commonly found in such workings have generally been neglected under the assumption that the radium has been transported in the mine waters and redeposited. The possibility for large-scale movement of radium in these sulfuric-acid-rich waters seems remote. The alternative interpretation that such radium concentrations are residual, and as such may indicate the presence of unleached uranium ore at greater depth within the walls, should be tested by deeper sampling.

Radium analyses, now a matter of routine in many laboratories, are necessary to establish the fact that the radioactive constituent of a given "hot spot" is radium and not one of several other radioactive elements belonging to the uranium and thorium series, all of which are much more readily transported in dilute H_2SO_4 solutions.

Many "hot spots," clearly of recent origin and generally assumed to be due to "transported" radium—in particular the high radioactivity shown by some rusted mine rails and nails—may be due to an original coprecipitation of iron oxides and ionium, the thorium daughter of U^{238}, which in turn decays to radium. Also the effects of the erratic and short-lived high radioactivity resulting from the occlusion of radon on moist dust and similar material are familiar to anyone who has made extensive radiometric surveys in uraniferous sulfide mines.

Where the analytical data show (1) that the high radioactivity of two or more samples from the same "hot spot" is due to radium and (2) that the radium is present in constant (but excessive) proportions to the uranium, the concentrations are almost certainly residual. In such cases the Ra/U ratio can be used to estimate, within the limits of the sampling, the amount of uranium lost from the exposed walls through leaching processes during the recent past, say within the last 50 years. Where predictions as to hidden uranium reserves of strongly leached mines must be based very largely on the results of shallow sampling, the quantitative implications of the Ra/U ratio may assume particular importance.

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GEOLOGY AND GEOCHEMISTRY OF BASE METAL DEPOSITS.

H. D. B. WILSON.

ABSTRACT.

The geochemical character and principles of distribution of the elements in igneous rocks are summarized. The geology and geochemistry of the base metals are then discussed in turn. Chromium and titanium are small lithophile ions related in size and distribution to ferric iron; thus they are concentrated in early magmatic differentiates associated with ultrabasic and basic rocks respectively. The thiophile elements nickel, copper, cobalt, zinc, and lead are concentrated in sulphide bodies. Immiscible sulphide deposits can separate only from ultrabasic and basic magmas because of the solubility of sulphur in silicate melts; hence the only thiophile elements that concentrate in the sulphide segregations are copper, nickel, and cobalt which are strongly concentrated in basic rocks and magmas. Nickel sulphide occurs almost entirely in these magmatic sulphide ores because of the small size of the nickel ion, but the somewhat larger cobalt and copper ions may be concentrated in hydrothermal as well as magmatic sulphide deposits. The hydrothermal deposits may be typed according to whether they are copper or copper-cobalt, copper-zinc, zinc-copper-lead, or lead-zinc deposits. Each type is associated with specific compositions of igneous rocks or magmas in which the elements are most concentrated because of their geochemical character and associations. Many of the principles outlined can be used in assessing deposits and areas for exploration and development.

INTRODUCTION.

It has long been recognized that the minor elements are associated with definite rock types. As early as 1913 Washington (38),[1] writing on the distribution of elements in the earth's crust, pointed out that not only were these minor elements related to general rock types but they were related to particular rocks in which some major element was abundant. Later studies have considerably changed and clarified our ideas concerning the association of elements, but in general the early work has been substantiated. The reason for these associations was not clear to the early workers because the associations had no apparent relationship to the positions of the elements in the periodic table or to the better known chemical properties of the elements.

In the last few years the principles of crystal chemistry have been applied to the study of minerals and to petrology. Crystal chemistry has shown the reasons for many of the associations observed empirically by early observers such as Washington and Vogt. A great many later authors have discussed the relationship of ore deposits to rock types; and Buddington (8) has summarized this subject and pointed out many of the complications.

This paper is designed to show the relation between Goldschmidt's geochemical principles, crystal chemistry, and base metal ore deposits, and to

[1] Numbers in parentheses refer to Bibliography at end of paper.

explain at least in part the reasons behind the association of ore deposits with particular rock types. As this paper is a generalized approach to the subject, many of the ideas will no doubt be changed with time, but the geochemical approach appears to give some system and coherence to many of the current theories regarding the origin of ore deposits.

CRYSTAL CHEMISTRY.

The principles of crystal chemistry used in the following discussion of the geochemistry of ore deposits, and Goldschmidt's (12) principles of the distribution of elements in minerals and rocks are briefly summarized in this section. Both sets of principles are treated in considerably more detail in the recent books on geochemistry by Rankama and Sahama (24) and Mason (18). The abbreviated description of the principles that follows concerns only ionic compounds, that is, those in which the atoms are in the ionized state and in which, consequently, the ions are held together by electrostatic attraction. An example is the NaCl structure in which the sodium gives up one electron to the chlorine resulting in an assemblage of Na^+ and Cl^- ions which are bonded by the electrostatic attraction of their opposite charges. The silicate and most of the oxide minerals have essentially this type of bonding.

Ionic crystals may be considered as a packing of spheres consisting of the various ions and the structure is determined by the relative numbers, relative sizes, and polarization properties of the ions involved.

Ionic Size.—The concept of ionic radius was first proposed by W. L. Bragg (6). He pointed out that although ions have no rigid boundary, "when two ions approach, a repulsive force which resists any closer approximation sets in with great abruptness near a certain value of the interatomic distance." Thus each ion has, in effect, a characteristic radius. Wasastjerna (37) deduced the size of the F^- and O^{2-} ions from refractivity measurements giving values of 1.33 Å and 1.32 Å respectively. Goldschmidt determined the ionic radius of the cations empirically by measuring the interatomic distances between oxygen or fluorine and a given cation, and using the above values for the anions. Pauling calculated the ionic radii using the effective nuclear charge and arrived at values close to Goldschmidt's. Pauling's value for O^{2-} is 1.40 Å. In this discussion the important point is that although the radii of the ions given by different authors vary slightly depending on the base of reference (the radius of O^{2-}) the radii almost invariably follow in the same ascending or descending order. The ionic radii used in this paper with the exception of Cu^{2+} are those given in Rankama and Sahama (24), Appendix 3, which are essentially those of Goldschmidt.

Coordination.—"Coordination" refers to the manner in which the ions or atoms of one type are arranged around another type. "Coordination number" is the number of atoms or ions of one type arranged around another.

The number of atoms that may surround any cation depends on the relative size of the two ions. Thus the ratio of the radius of the cation to that of the anion determines the coordination in ionic crystals. As oxygen is the

common anion in the silicate and oxide minerals, the radius ratio of the cation to oxygen commonly determines the coordination.

The relation between radius ratio and coordination number for two sizes of spheres is shown in Table I.

Coordination affects ionic size but the effect is not large and is similar on all ions. For example, an ion with radius of 1.00 Å with coordination of 6 will increase in size to 1.03 Å with a coordination of 8 (Wells 39). The ionic radii used in this paper are those for a coordination number of six.

Pauling's Rule of Valency.—Pauling (23) pointed out that in ionic crystals the law of valency is satisfied by making the total positive and negative charges equal. This is not brought about by pairing off individual positive and negative ions. Pauling's rule is stated as follows: "Divide the valency of a given positive ion by the number of surrounding negative ions. The resulting fraction is the contribution of the positive ion towards satisfying the valency of each negative ion. If we now consider a given negative ion, it is found that the sum of the contributions from its neighboring positive ions is equal or approximately equal to its valency."

TABLE I.

Coordination	Arrangement of larger spheres around smaller	Radius ratio
2	Linear	0–0.15
3	Triangular	0.15–0.22
4	Tetrahedral	0.22–0.41
6	Octahedral	0.41–0.73
8	Cubic	0.73–1.00
12	Cubo-octahedral	1.00 and above

This imposes strict conditions on the substitution of ions in crystals if the substituting ions have different valencies. For example, to substitute a Ca^{2+} ion for an Na^{1+} ion in feldspar, an Al^{3+} ion must also be substituted for an Si^{4+} ion to keep the total positive charge the same. Also only an ion in 8-fold coordination can be substituted for the Na^{1+} or Ca^{2+} (0.98 and 1.06 Å) in plagioclase and consequently we cannot substitute Mg^{2+} or Fe^{2+} for example, as these are such a size (0.78 and 0.83 Å) as to require 6-fold coordination and the structure may not be able to contract to make this a stable form.

Goldschmidt's Rules.—Goldschmidt (12) formulated three important rules bearing on the geochemistry of ionic crystals.

a. A given crystal structure is such that only ions of a limited range in size may enter any particular part of that structure. Thus two ions of identical size and possessing the same valency may enter the structure in a given position with equal ease if the size is appropriate for such ions.

Goldschmidt uses the example of nickel and magnesium which have identical ionic radii (0.78 Å) and the same valence. Although they differ greatly in chemical properties they may readily substitute for each other in ionic crystals.

b. If two ions have almost the same radius, the smaller one will form the tighter bond. In the case of crystallization from a melt the smaller ion will be concentrated in early crystals of an isomorphous series. Goldschmidt

cites the example of Mg^{2+} (0.78 Å) and Fe^{2+} (0.83 Å) in the ferromagnesian minerals.

c. If two elements have the same ionic radius but different valency, the ion with the greater valence forms the tighter bond and would be enriched in early formed crystals in an isomorphous series.

Isomorphism.—Two elements with similar ionic radii may form a mixed crystal series if the structure can, at the same time, adjust for any difference in valence as in the plagioclases. The limits within which the radii of the ions may differ and still form a stable mixed crystal series at normal temperature and pressure have been roughly established at 15 percent of the smaller radius. At high temperatures the ionic radii may differ by a larger amount and still form an isomorphous series.

Distribution of Elements in Liquids and Solids.—Goldschmidt (12) determined the affinities of the elements for the various types of earth material by studying the distribution of the elements in meteorites and in mattes and slags. He found that elements will enter preferentially an iron phase, a sulphide phase, or a silicate phase and he described elements of the first type as siderophile, of the second as chalcophile, and the third as lithophile. Shand (28) has suggested thiophile in place of chalcophile, a change adopted in this paper.

Goldschmidt also found that the partition of the elements into these three phases depends upon the arrangement of the orbital electrons in the electron shell structure of the particular ion. Those elements with ions of the rare gas type enter the silicate phase, as, for example, Na^{1+}, Ca^{2+}, Al^{3+}. The elements whose ions have a complete outer sub-shell containing ten electrons enter the sulphide phase. The transitional elements whose ions have an incomplete outer electron shell enter the iron phase. If an iron phase is absent the later group of elements apparently enter a sulphide phase in preference to a silicate phase. This partition of the elements takes place at any time that an element must be distributed between any of the two phases.

THE MAJOR ROCK-FORMING MINERALS.

The geochemistry of the major rock-forming elements is considered briefly because the distribution of each minor, but economic element, is related to the distribution of a specific major element or elements.

In all silicate structures, the small silicon is surrounded by four oxygens at the corners of a tetrahedron and the structures are dominated by these SiO_4 tetrahedra. The tetrahedra may be linked in several different ways, but each species or group of species has a characteristic type of linkage. Bragg (7) arrived at a structural classification of the silicates by using the type of silicon-oxygen linkage. He started with isolated tetrahedra and proceeded through groups of structures of minerals with the tetrahedra linked into separate Si-O complexes, into one-dimensional chains, into two-dimensional sheets, and finally into three-dimensional frameworks. The portion of the classification that includes the common rock-forming minerals is as follows:

(1) Separate $(SiO_4)^{4-}$ groups. The olivines. $(Mg, Fe)_2 [SiO_4]$.
(2) Single Si-O chains formed by linking tetrahedra corner to corner in an endless row (one-dimensional framework). The pyroxenes. $(Mg, Fe) [SiO_3]$.
(3) Double Si-O chains formed by linking two of the single chains (essentially one-dimensional linkage). The amphiboles. $Ca_2Mg_5 [Si_8 O_{22}] OH_2$.
(4) Si-O sheets formed by linking three corners of each tetrahedron to neighbors to form completed sheets. The micas. $KMg_3 [AlSi_3O_{10}] OH_2$.
(5) Continuous three-dimensional frameworks formed by linking all four corners of each tetrahedron to neighbors. Feldspars and quartz. $K[AlSi_3O_8]$.

The order of crystallization of the rock-forming minerals was established empirically by Rosenbusch, and Bowen, using experimental as well as empirical relationships, worked out the well known reaction series. The similarity of Bragg's silicate structure classification to Bowen's discontinuous reaction series is obvious, so apparently some relationship exists between the two series.

Figure 1 shows that the common cations fall into groups of similar sized ions, and it is apparent that the common rock-forming mineral groups correspond to these ionic groups. It is also apparent that the order of crystallization corresponds to the increasing size of the cations, that is, the small ions tend to crystallize early.

Considering the major cations in order of size, we find that silicon has the smallest radius. Because of its small size, high charge and abundance, it crystallizes throughout the whole period of crystallization and as already stated it forms the tightly bonded silicon-oxygen tetrahedra which are the basic structural units of all the silicate minerals.

Alumium plays a dual role in silicate structures because of its ionic radius. The radius ratio of aluminum : oxygen is close to the boundary of four- and six-fold coordination; thus aluminum may replace silicon in the tetrahedra in four-fold coordination, or some of the aluminum may enter other parts of silicate or oxide structure in six-fold coordination replacing such ions as Cr^{3+}, Fe^{3+}, Mg^{2+}, and Fe^{3+}.

The other major rock-forming elements fall, as we have just seen, into natural groups according to their ionic size. Elements having ions of similar size form completely isomorphous groups of minerals. Ions differing by more than about 15 percent may form limited isomorphous series but usually form new mineral groups.

The generally early crystallizing "iron ore" minerals are oxides of the small ions Fe^{3+}, Mg^{2+} and Fe^{2+} mainly, although other minor elements of suitable size may replace these major elements to some extent.

Mg^{2+} and Fe^{2+} and the silicon-oxygen tetrahedra are the characteristic elements of the ferromagnesian group of minerals. Olivine and orthorhombic pyroxene are the early-formed ferromagnesian minerals stable at high tem-

perature. They contain only the silicon-oxygen tetrahedra, and Mg^{2+} and Fe^{2+} in approximate six-fold coordination. Olivine with the simplest structure forms first, the smaller magnesium ions being concentrated with respect to iron in the early crystals. The later-crystallizing monoclinic pyroxenes, amphiboles and micas have progressively more complicated structures.

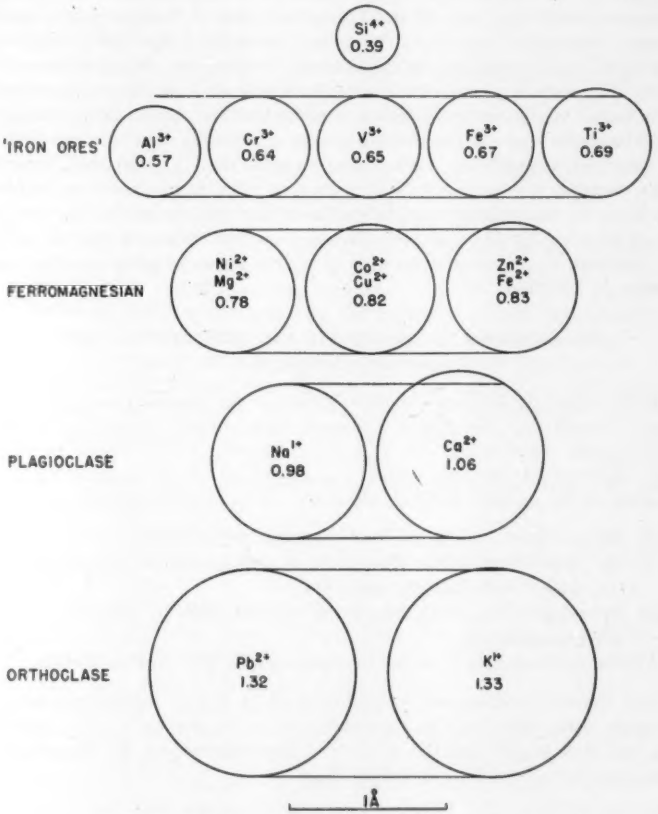


FIG. 1. Relative size of the common metallic ions.

Slightly larger ions such as Na^{1+} and Ca^{2+} whose similar radius ratios with respect to oxygen are on the border of six-fold and eight-fold coordination may be admitted to the lattice to form several species with limited amounts of isomorphism.

The third important series based on the size of the ions is the isomorphous calcium-sodium plagioclase feldspars. Calcium and sodium have similar

ionic radii and their aluminum silicates form an almost complete mixed crystal series with calcium and sodium in approximate eight-fold coordination. Calcium is a larger ion than sodium but because the electric charge of calcium is twice that of sodium, calcium is concentrated in the early formed plagioclase crystals.

Potassium is similar to sodium chemically but because the size disparity of its ion is considerably beyond the 15 percent limit, it is not readily admitted into the plagioclase lattice, and it characteristically forms the potash series of feldspars with potassium in approximate twelve-fold coordination.

The micas are in part an interesting exception to some of the general rules. K^{1+} is found in the ferromagnesian mineral biotite. Muscovite contains the small aluminum ion whereas biotite contains the larger magnesium and iron ions and yet crystallizes earlier than muscovite. The crystal structures readily explain the apparent discrepancies. The potassium ions occur in large holes in the structure so the radius of the potassium ion has no effect. Al^{3+} substituting for Mg^{2+} or Fe^{2+} takes up only two-thirds of the magnesium-iron positions, the remainder remaining vacant, thus the general rules of substitution do not hold.

GEOCHEMISTRY, DISTRIBUTION, AND ECONOMIC GEOLOGY OF THE BASE METALS.

In the following sections the distribution of the elements and character of the ore deposits of the major economic base metals chromium, titanium, nickel, copper, cobalt, zinc, and lead are discussed. A discussion of sulphur is also included at the appropriate place because of its significance in the formation of the metallic sulphide deposits. The writer's purpose is to show

(1) the geochemical character of the base metal elements;
(2) the distribution of the elements in igneous rocks and their relation to the major rock-forming elements;
(3) the relation of ore deposits to the igneous rocks in which the elements are concentrated;
(4) the characteristics of the ore deposits of the various metals.

Each element is discussed individually or in closely related groups. An attempt is also made to show the relation of each element to the other elements and it is hoped that the relation of the elements to the magmatic and hydrothermal types of deposit will be clear.

THE MAGMATIC OXIDE MINERALS.

Geochemistry.

The ions Cr^{3+}, Fe^{3+}, V^{3+}, and Ti^{3+} have similar ionic radii and thus form a group of mixed crystals when crystallizing from a magma. Crystals containing these elements should occur relatively early in a differentiated series of igneous rocks because the elements all have a relatively small ionic radius and because iron is one of the abundant elements in the earth and in magmas.

As the ionic radii of the elements are small, they apparently can, under certain conditions, compete with silica to form oxides, although they do not replace silica to any extent in the silicon-oxygen tetrahedra.

Chromium, vanadium, and titanium are lithophile elements so they would remain in the silicate magma even if a sulphide melt separated from the silicate. Iron is siderophile or thiophile but because it is so much more abundant than sulphur in a normal magma most of the iron must remain in the silicate-oxide liquid along with the chromium, vanadium and titanium. The elements in this group therefore remain essentially in the silicate liquid and crystallize from that liquid even if a sulphide liquid or segregation forms from the magma and removes a portion of the iron.

The ionic radii of this group of elements increase from Cr^{3+} (0.64 Å), through V^{3+} (0.65 Å), Fe^{3+} (0.67 Å), and Ti^{3+} (0.69 Å); hence chromium should be enriched in early formed crystals and titanium in later crystals of an isomorphous series formed from this group of elements.

The crystal structures and geological associations of the minerals of these oxides are not yet thoroughly understood. The spinel type structure with approximate cubic closest packing appears to be the stable form with the smallest cations of this group and with the larger cations at high temperature, but the hematite-ilmenite structure with approximate hexagonal closest packing appears more stable with the largest cations at lower temperatures.

Al^{3+} (0.57 Å) is intermediate in size between the silicon and chromium ions. Because this radius is within the limits of isomorphous substitution with Cr^{3+}, aluminum must also be considered in the discussion of the magmatic oxide minerals. Al^{3+} may also substitute for Si^{4+} in the silicon-oxygen tetrahedra. As Al^{3+} is even smaller than Cr^{3+}, aluminum should be concentrated in early spinel crystals.

Spinel contains a divalent group of cations in its formula ($RO.R_2O_3$), in addition to the trivalent group of ions. This divalent group is usually represented by FeO and MgO. Mg^{2+} (0.78 Å) has a smaller radius than Fe^{2+} (0.83 Å); therefore magnesium should be concentrated with respect to iron in early formed crystals. Less abundant metals of suitable ionic radius and valence, such as nickel, might also enter this part of the spinel structure, and again, depending upon ionic radius and valence, these metals should be enriched in either early or late formed crystals.

Summarizing, therefore we should expect that the magmatic oxides crystallizing with the first formed, most basic rocks, would be high in trivalent aluminum and chromium, and divalent magnesium. As crystallization proceeds and later oxide segregations are formed, the later segregations would contain more and more ferrous and ferric iron and titanium, and less and less aluminum, chromium and magnesium. Thus in chromite segregations in ultrabasic rocks the presence of aluminum tends to decrease the chromium content of chromite, but the high magnesium : ferrous iron ratio tends to maintain a high chromium : iron ratio. The end member mineral chromite of composition $FeO.Cr_2O_3$ cannot occur as a magmatic mineral because chromite crystallizating from a natural magma will always contain considerable aluminum and magnesium.

Geology of the Magmatic Oxide Mineral Deposits.

It is of interest to compare the theoretical occurrence of this oxide group of elements with the actual occurrence in natural deposits. Magmatic chromite, magnetite, and ilmenite have usually been considered as unrelated mineral deposits. It is proposed to show that the deposits are related as a gradational series and that the composition of each deposit corresponds to the composition of the related silicate rocks, because the composition of both oxides and silicates is related to the stage of differentiation. Chromite magnetite and ilmenite are first considered separately to bring out the similar characteristics of the deposits and their related rock type. The distribution of the elements in rock types and in the oxide minerals in the Bushveld lopolith and other intrusives is used to draw the whole picture together.

Chromite.—The association of chromite with ultrabasic rocks is well established. The ore deposits occur within, or at the boundary of the related ultrabasic intrusion. Most characteristically, they occur at some particular horizon or zone in the intrusion. Chromite deposits are of two principal types: flat stratiform bands which may be continuous for several miles in layered intrusives; and large irregular pods or "sackiform" bodies which generally roughly parallel the margins of the intrusive rock body containing them. In a few deposits, part of the chromite ore follows definite fissures in the ultrabasic intrusion. Examples of the fissure controlled type include some of the ore at Selukwe, Southern Rhodesia (25), Briggs Creek, Oregon (2), and Quebec, Canada (30). However the close spatial relationship between ore and intrusive is maintained even with this type as the ore does not migrate beyond the margins of the intrusive; thus the chromium does not have the mobility characteristic of the elements in typical hydrothermal deposits.

The composition of the chromite in any one ore body is relatively constant, although the chromite in different ore bodies in the same intrusive may differ in chrome content. This fact is clearly shown in the chromitite horizons in the Bushveld complex where washed chromite from any particular band contains a constant amount of chromium and a constant chrome : iron ratio. For example, the washed chromite from the "New Seam" at the Zwartkop Chrome Mine consistently contains 53% to 54% Cr_2O_3 over a strike length of more than two miles.[2] Similarly the washed chromite from the "Old Seam" assays 49% to 50% Cr_2O_3 and the "Upper Seam" 44% to 45% Cr_2O_3. In general the chromitite seams of the Bushveld are in the 42–52% Cr_2O_3 range, but individual seams have a very consistent chromium composition, remaining within one or two percent of the average content for the particular seam. The chromitite seams from the Bushveld complex are ideal examples, but the principle of relative constancy of the mineral composition in a single segregation appears to be general, with only the slight changes in composition from top to bottom of a single band as shown by van der Walt (32). The chromite from the Bird River sill, Manitoba, consistently carries from 36–40% Cr_2O_3 with a 1.2 : 1 chrome-iron ratio. High grade (50% Cr_2O_3)

[2] Oral communication from Mine Manager.

or high chrome-iron ratio (3:1) chromite has not been found in the chromite horizon of the Bird River sill. The Stillwater chromite carries 44–48% Cr_2O_3 (29) with a chromium:iron ratio of 1.5:1 to 1.9:1. Ratios of 1:1 or 3:1 are not found in this deposit. Similarly other chromite ore bodies are consistently high-grade ores or low-grade ores with a constant chromium:iron ratio.

Titaniferous Magnetite.—Titaniferous magnetite bodies occur in gabbroic intrusives in a similar manner to the chromite deposits in the ultrabasic intrusives. For example, the magnetite horizons of the Bushveld complex are well defined layers similar to the chromitite layers in appearance and geological relationships except that the magnetite horizons occur in the upper part of the main norite zone close to the granophyre, whereas the chromite layers occur in the ultrabasic zone in the lower part of the intrusive.

The titaniferous magnetite zone on the south range of the Sudbury norite occurs at a similar horizon to the titaniferous magnetite of the Bushveld, that is, in the norite a few hundred feet below the transition to micropegmatite. Unlike the sharply defined Bushveld magnetite horizons, the Sudbury magnetite occurs disseminated in the norite in a zone that may be as much as a thousand feet wide. Most of the Sudbury norite is magnetite free, but in the magnetite zone, norite samples consistently ca.ry from two to fifteen percent magnetite. The zone of magnetite concentration begins abruptly in any section. It is continuous along strike but its width is not constant as it may bulge or thin considerably.

The titaniferous magnetite zone at Sudbury is also an apatite zone, and on the South Range there is almost as much apatite as magnetite present in the rock. Beyond this zone the gabbro is generally free of apatite. The association of phosphorus and titanium during crystallization has been noted by Vogt (35).

Titaniferous magnetite zones have been noted in many other basic bodies both in large lopoliths such as the Duluth gabbro and in smaller relatively undifferentiated looking noritic and gabbroic bodies in the Sudbury district. The geological occurrence of the titaniferous magnetite in basic intrusives is thus similar to that of chromite but the two ore types are related to intrusive rocks of differing composition.

The titaniferous magnetites like the chromites are apparently relatively constant in composition in any one deposit, that is, the titanium:iron ratio remains relatively constant and the ratio depends upon location within an intrusive if the intrusive is differentiated. The ratio also must depend on the inital titanium and iron content of the original magma; for example, the analyses of plateau basalts from different regions show a 500 percent variation in titania content.

A sample of the ilmenite-bearing titaniferous magnetite from one of the middle magnetite horizons of the Bushveld complex was heated for three hours at 970° C, then quenched. A comparison of the polished sections of the material before and after heating showed that the ilmenite dissolved completely

into the magnetite structure. It seems therefore that the titaniferous magnetite-ilmenite mixture now present in the magnetite band was precipitated from the magma entirely with the spinel-type structure, with ilmenite separating out as the solid slowly cooled.

Ilmenite.—The Allard Lake titanium deposits are some of the best known ilmenite deposits. Hammond (13) has described them in general as flat lying tabular bodies. In a later paper (14) he states that the ilmenite may also occur in narrow dikes or irregular lenses, but all the ilmenite occurs within anorthositic rocks. The similarities of these ilmenite bodies to the sill-like, the sackiform, and the dike-like occurrences of chromite are obvious.

TABLE II.

CONCENTRATIONS OF THE ELEMENTS IN ROCK TYPES.

Ion	Ionic radius	Concentration, g/ton (or p.p.m.)				
		Peridotite	Gabbro	Diorite	Granodiorite	Granite
Cr^{3+}	0.64	3400	340	68		2
V^{3+}	0.65	17	56			17
Fe^{3+}	0.67	21500	22100	22100	12300	11000
Ti^{3+}	0.69	4200	5810	5040	3400	2300
Ni^{2+}	0.78	3160	158	40		2.4
Mg^{2+}	0.78	205000	45300	25200	11500	5300
Cu^{2+}	0.82		149	38		16
Co^{2+}	0.82	237	79	32		8
Fe^{2+}	0.83	58400	46300	34200	20600	13800
Zn^{2+}	0.83		90	120	200	30
Ca^{2+}	1.06	27100	78500	48100	31600	14200
Na^{1+}	0.98	4000	18900	25200	27400	25800
Pb^{2+}	1.32		5			30
K^{1+}	1.33	2150	7400	17600	22800	34100

Sources of Table II:

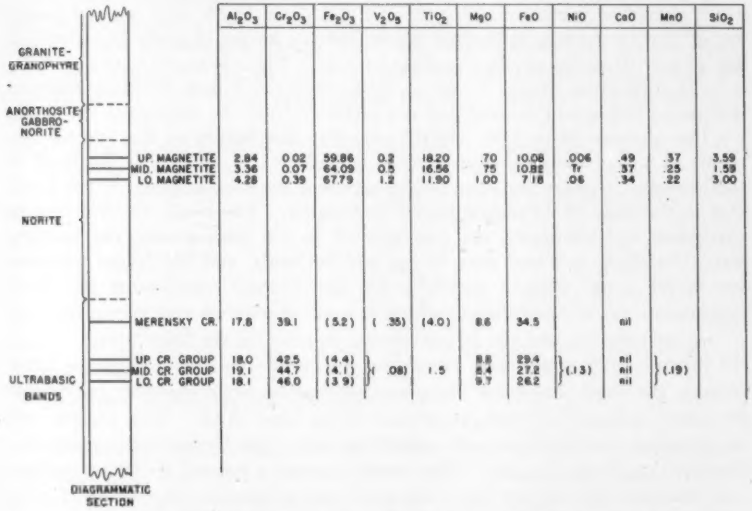
Fe^{2+}, Ti, Mg, Fe^{3+}, Ca, Na, and K from Daly (11).
Cr, Ni, and Co from Goldschmidt (12).
Cu from Sandell and Goldich (26).
V from Rankama and Sahama (24).
Zn from Lundegårdh (17).
Pb from Hevesy, Hobbie and Holmes (15).

Ionic radii for 6-fold coordination from Rankama and Sahama (24) except Cu^{2+} which Rankama and Sahama give as only approximate. Ahrens (1) gives Cu^{2+} same as Co^{2+} and .02 Å less than Fe^{2+} and Zn^{2+}.

Hammond has also stated that all known ilmenite bodies occur with gabbro and anorthosite. At Allard Lake the ore containing 32% TiO_2 is associated with anorthosite in which the feldspar ranges from andesine to sodic labradorite. The iron-titanium ratio of the ore is relatively constant as shown by several hundred analyses. The conclusion seems to be valid that ilmenite ore bodies are similar to chromite bodies in structure, constancy of composition, and location within an intrusive of related composition, but ilmenite ore bodies in general are associated with much later differentiates than are chromite ore bodies.

The Distribution of Chromium, Vanadium, Ferric Iron, and Titanium in Igneous Rocks

The distribution of chromium, vanadium, ferric iron and titanium in igneous rocks is shown in Table II. Chromium is highly concentrated in ultrabasic rocks. Wager and Mitchell (36) and Nockolds and Mitchell (21) have shown that chromium is most concentrated in the early differentiates of the Skaergaard and Glen Fyne intrusives with rapid tapering off in chromium content in the later differentiates. The basic rocks of the Glen Fyne complex contain only about one eighth of the chromium content of the ultrabasic members. Vanadium and titanium on the other hand reach their greatest concentration in the basic rocks.



	Al_2O_3	Cr_2O_3	Fe_2O_3	V_2O_5	TiO_2	MgO	FeO	NiO	CaO	MnO	SiO_2
UP. MAGNETITE	2.84	0.02	59.86	0.2	18.20	.70	10.08	.006	.49	.37	3.59
MID. MAGNETITE	3.36	0.07	64.09	0.5	16.56	.75	10.82	Tr	.37	.25	1.59
LO. MAGNETITE	4.28	0.39	67.79	1.2	11.90	1.00	7.18	.06	.34	.22	3.00
MERENSKY CR.	17.8	39.1	(5.2)	(.35)	(4.0)	8.6	34.5		nil		
UP. CR. GROUP	18.0	42.5	(4.4)			8.8	29.4		nil		
MID. CR. GROUP	19.1	44.7	(4.1)	(.08)	1.5	8.4	27.2	(.13)	nil	(.19)	
LO. CR. GROUP	18.1	46.0	(3.9)			9.7	26.2		nil		

FIG. 2. Composition of the oxide layers of the Bushveld Complex.

Sources: The analyses of the magnetite bands are averages of all the analyses of the three magnetite bands given in Schwellnus and Willemse's Table I (27). The analyses of the lower, middle and upper chromite groups are averages of the composition of all the chromite bands in each group as given by van der Walt (32). van der Walt included all iron under FeO. The bracketed analyses are from other sources so should not be added to the van der Walt totals. The figures for Fe_2O_3 are based on another similar series of bands so are not directly comparable, but show the trend. The analyses for titanium in the Merensky chromite, and for nickel and manganese in a composite sample of the chromite horizons were made by the Manitoba Mines Branch. It is probable that van der Walt's analyses for Al_2O_3 in the Merensky chromite should be corrected for the TiO_2 content as he did not separate the aluminum and titanium in this analysis. The determinations of V_2O_5 in the chromite in the Merensky horizon and in the composite sample of the chromite horizons were made at the Rock Analysis Laboratory of the University of Minnesota, using samples supplied by the author.

The Serial Relationships of the Magmatic Oxide Deposits.

The key to the serial relationship of the magmatic oxide bodies and the related silicate rocks is supplied by the Bushveld complex. This basin-shaped intrusive is more than 200 miles long, 80 miles wide and several miles thick. It is highly differentiated so that it now appears as a layered series with ultrabasic rocks at the bottom ranging upward through norites, gabbros and anorthosites to the granites at the top. Oxide bands occur at a number of horizons in this layered series and the present investigation throws much light on the relations between the composition of the oxide in any band and that of the adjacent rock layer, and also on the extent to which the composition of the oxide is dependent on the position of the band in the intrusive as a whole. Analyses of the oxide layers are given in Figure 2.

It should be pointed out that the analyses given in the table are not analyses of the chromite in individual bands, but are averaged analyses representing groups or series of closely spaced bands. The composition of the chromite in individual bands of such a series may not follow in strict order of decreasing chromium content, but the variation from the average is not great.

The analyses show very clearly how the distribution of the several elements in any of the oxide bands is controlled by the position of the band in the intrusive complex and thus by the nature of the rock adjacent to the band, that is, the stage of differentiation of the magma. The small trivalent ions of chromium and aluminum are concentrated in the early bands, the medium sized vanadium and iron ions in the middle bands, and the larger titanium ion in the upper bands. Similarly for the divalent constituents the small magnesium ion is concentrated with the small aluminum and chromium ions in the early bands, and the larger ferrous iron ion in the later bands. Even the minor metals which may enter into the oxide structure follow the same pattern, the small nickel ion being concentrated in early chromite bands and the larger calcium and manganese ions in the later bands. The pattern and relationships are therefore well established with high chromium chromite related to the ultrabasic rock. The earlier a band is formed in the crystallization sequence, the higher the chromium content and the higher the Cr/Fe ratio.

The titaniferous iron ores are characteristic of norites and the titanium ores of gabbros and anorthosites. These are the patterns that actually occur in nature and they are the patterns predicted from known crystal chemistry principles.

Some of the Canadian chromite occurrences may be used to check the Bushveld occurrences, to show that the pattern is consistent. The Bird River chromite bands occur in serpentinized peridotite about 60 feet below the contact of this rock with overlying gabbro, that is, in a position roughly corresponding to that of the Merensky horizon in the Bushveld complex. The similarity in composition between the Bird River chromite which contains 40% Cr_2O_3 and the chromite of the Merensky and Upper Chrome groups of the Bushveld complex is apparent from the analyses in Figure 2,

that is, 39% Cr_2O_3 in the Merensky horizon. The Cr/Fe ratios are about 1.3:1 in Bird River chromite and 1:1 in Merensky chromite.

As stated previously a band of norite containing titaniferous magnetite occurs on the South Range of the Sudbury intrusive. This band is from about 500 to 1,000 feet in thickness and its top is from 500 to 1,000 feet below the micropegmatite contact. Its position therefore roughly corresponds to that of the "massive magnetite" horizons of the Bushveld complex. The Sudbury magnetite band contains disseminated magnetite and ilmenite making up from 2 to 15 percent of the total rock. A concentrate of the black oxides assayed by the Manitoba Mines Branch contained 0.37% Cr_2O_3 and 17% TiO_2. The composition is therefore comparable to the Bushveld magnetite horizon.

The Lac Tio ilmenite deposit at Allard Lake, Quebec, occurs as a flat-lying tabular body in anorthosite and contains 32% TiO_2 (14). It thus occurs in a type of rock that, in the Bushveld complex lies above the top magnetite horizon. The pattern thus appears consistent with what would be expected whether the orebodies are bands or pods, massive or disseminated.

TABLE III.*

COMPARISON OF WESTERN HEMISPHERE CHROMITES.

	Average of 45 chromites	Average of 5 Caspar Mt. chromites
Cr_2O_3	48.8	25.7
Al_2O_3	16.7	4.7
Fe_2O_3	5.64	39.5
FeO	14.5	24.7
MgO	13.0	2.1
MnO	.18	.3
CaO	.12	.3
TiO_2	.33	1.6
SiO_2	.36	.5

* Data from Average of Stevens (29) analyses.

Further confirmation of the distribution of the elements in chromites may be had from the analyses by Stevens (29). Table III, a comparison of high-grade chromite with the low-grade chromite from Caspar Mountain, Wyoming, shows that the low-grade chromite contains lesser amounts of the small aluminum and magnesium ions and larger amounts of the larger iron, titanium, manganese, and calcium ions.

Thayer (31) also stated that high grade chromites with high chromium content and high chromium-iron ratios are found associated with dunites and serpentines, whereas lower-chromium, high-iron chromites are associated with pyroxene-rich peridotites.

NICKEL.

Geochemistry.—Ni^{2+} has the same ionic radius and valency as Mg^{2+} (0.78 Å). The ionic radius of Fe^{2+} is 0.83 Å, thus in a crystallizing silicate system the minor element nickel should be concentrated with the magnesium in the early formed crystals of the isomorphous ferromagnesian minerals.

The outer electron shell structure of Ni^{2+} is such that it preferentially enters a sulphide phase if a sulphide liquid separates from a silicate liquid. Mg^{2+}, on the other hand, having a rare gas type of electron shell should remain in the silicate phase if a sulphide phase separates. Nickel and magnesium, which concentrate together in a crystallizing silicate melt, will therefore be separated if a sulphide liquid separates from a silicate magma. This separation may take place either in a completely liquid stage or in a partly crystallized mixture as it has been determined experimentally that liquid iron sulphides will extract nickel from olivine crystals suspended in the melt.

Geology of Nickel and Nickel Ore Bodies.—Nickel-copper ore bodies may not appear to have much in common with chromite ore bodies, but a close examination shows that they do have many features in common. These similarities suggest that nickel-copper deposits like chromite deposits are of magmatic origin. Comparing nickel-suphide deposits with chromite deposits it may be seen that (i) nickel in the sulphides in any one ore body is constant as is chromium in the oxides, (ii) the grade of nickel in the sulphides corresponds directly to the rock type and decreases with decreasing acidity of the associated rock, as does chromium in the chromites, (iii) nickel sulphides like chromite deposits are associated with specific intrusives and show a lack of mobility in that they occur within or alongside of their related intrusive, (iv) the deposits have a relatively constant spatial relation to the related intrusive, nickel sulphides at or near the base, chromite at some particular horizon or horizons in the intrusive. The differences in the type of deposits are due to the oxyphile character of chromium and its ionic radius in relation to ferric iron and the thiophile character of nickel and its ionic radius in relation to that of the major element magnesium, all of which depends on the structure of the ions themselves.

The distribution of nickel in silicate minerals and rocks is now well known. Vogt (34) showed that the nickel content was highest in the ultrabasic rocks and decreased progressively in more acid rocks. He also showed that of the igneous silicate minerals, olivine contained the most nickel and the content decreased progressively in enstatite, monoclinic pyroxene, amphibole, and biotite; and feldspars and feldspathoids were lacking in nickel. Many other authors such as Goldschmidt (12), Wager and Mitchell (36), and Nockolds and Mitchell (21) have confirmed Vogt's work in other areas and clearly established the concentration of nickel in the early magmatic differentiates, and have pointed out the similar distribution of nickel and magnesium in silicate rocks and minerals (Figs. 3 and 4). Estimates of the nickel content of rocks are shown in Table II.

The amount of nickel in the sulphide is constant in any nickel sulphide ore body. For example the Frood ore body at Sudbury has a pyrrhotite: pentlandite ratio of 5.4 to 1.[3] All drill holes in the mine have similar pyrrhotite: pentlandite or sulphur: nickel ratios. The sulphur: nickel ratio of almost all holes lies in the range of 5: 1 to 6: 1, and the average of each section of the mine is consistent. Even units as small as hand specimens always show the characteristic sulphur: nickel ratio of the whole ore body.

[3] Can. Min. Jour. 1946.

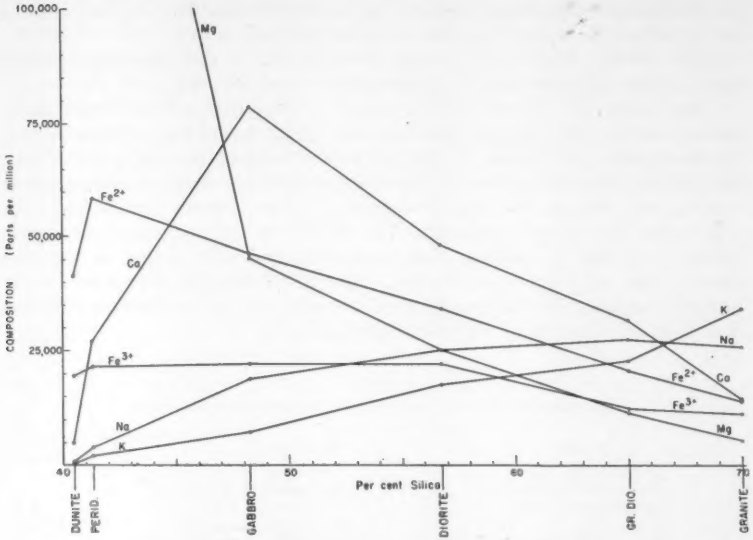


FIG. 3. Silica variation diagram showing the average major element composition of the principal igneous rock types. From averages of Daly's analyses (11). The analyses of kimberlite were not included with the peridotites because of their fragmental nature.

TABLE IV.

PYRRHOTITE : PENTLANDITE RATIOS OF SUDBURY MINES.

	Pyrrhotite	:	Pentlandite
Frood	5.4		1
Creighton	3.4		1
Levack	5.0		1
Garson	4.7		1
Murray	6.6		1

The sulphur : nickel ratio, however, is slightly different but characteristic for each ore body, that is to say, the pure sulphide ore contains a constant amount of nickel. At Sudbury the pyrrhotite : pentlandite ratios for different mines are shown in Table IV.[4] It should also be noted that the sulphur : nickel ratio is constant in all types of ore at a single mine, whether it occurs as massive ore, as disseminated blebs in fresh hypersthene norite, as disseminated blebs in altered uralitized norite, as ore along fault zones, as replaced schist, or in fractures in gabbro and granite country rocks.

Vogt (34) showed that in Scandinavian nickel deposits, the amount of nickel in the sulphide in an ore body was related to the type of rock in which the ore occurred. The sulphide in ultrabasic rocks contained the largest amounts of nickel with the nickel content decreasing with increasing acidity

[4] Can. Min. Jour. 1946.

or decreasing magnesia content. Vogt's observations are confirmed by a study of Canadian nickel deposits as shown in Table V.

The relation of the grade of the ore minerals to the associated igneous rock is thus a feature of both nickel and chromite deposits.

Newhouse (20) showed the distribution of the minor primary sulphides in igneous rocks. Newhouse's data show that 48 percent of the sulphide-bearing norites contain pentlandite, 34 percent of the sulphide-bearing gabbros contain pentlandite, 14 percent of the sulphide-bearing diorites contain pentlandite, and none of the sulphide-bearing granites contain pentlandite. He also found that where pentlandite does occur the ratio of pentlandite: pyrrhotite is smaller in gabbros than in norites, and still smaller in the two diorites that did contain pentlandite. The distribution of the nickel in the primary sulphides of igneous rocks is thus similar to the distribution of nickel in ore deposits related to particular igneous bodies.

TABLE V.

RELATION OF NICKEL CONTENT OF SULPHIDE TO ROCK TYPE.

Locality*	Rock type	Maximum % nickel in the sulphide
Werner Lake, Ont.	Peridotite	10.0
Rankin Inlet, N.W.T.	Serpentine	10.0
Shebandowan, Ont.	Peridotite	9.0
Alexo, Ont.	Peridotite	8.0
Bruvand, Norway	Peridotite	7.0
Choate, B. C.	Pyroxenite	5.0+
Espedelen, Norway	Pyroxenite	4.5
Hosanger, Norway	Norite	6.5
Sudbury, Ont.	Norite	3.0–6.0
Rice Island, Manitoba	Norite	5.0
Herb Bay, Man.	Norite	4.0
Bamle, Norway	Norite	3.75–4.0
Romsaas, Norway	Norite	3.5–3.75
Yakobi Island, Alaska	Norite	3.0
Klefva, Sweden	Norite	2.6
Lake Athabaska, Sask.	Diorite	1.0
Chibougamou, Que.	Anorthosite	0.5

* The data for the Scandinavian deposits are those of Vogt (34).

The physical relation of the copper-nickel sulphide bodies to the related intrusive distinguishes the copper-nickel deposits from typical hydrothermal deposits. The most characteristic location for copper-nickel sulphide deposits is on the basal contact, that is, the bottom of the intrusion to which they are related in composition. This condition is found at Sudbury, Ontario; Rankin Inlet, N.W.T.; Shebandowan, Ontario; Alexo, Ontario; Rice Island, Manitoba; Yakobi Island, Alaska; Lobster Bay, Quebec; Gap mine, Pennsylvania; the Logan sills, Ontario; Insizwa South Africa; and in the numerous Norwegian deposits. In a few localities the copper-nickel sulphides occur in dikes. The sulphides may be disseminated throughout the dikes or occur in massive bodies at the borders of the dikes or completely within the dikes. In the Bushveld and Great Dike intrusives, copper-nickel sulphides occur in definite horizons such as the Merensky horizon, and in sulphide pipes near the base of the intrusive. In a very few stock-like intrusives such as at Lynn

Lake, Manitoba, the ore occurs in the norite, near but not at the base, and in bodies subparallel to the lower contact of a steeply dipping intrusive. All minable nickel-sulphide bodies are directly associated with a basic intrusive of related composition and the vast majority of the ore bodies are along the basal contact of the intrusive.

The major control of the loci of nickel-copper deposits is at the basal contact of a high magnesia intrusive. Other controls such as downward embayments and fault structures are also important. A glance at a detailed

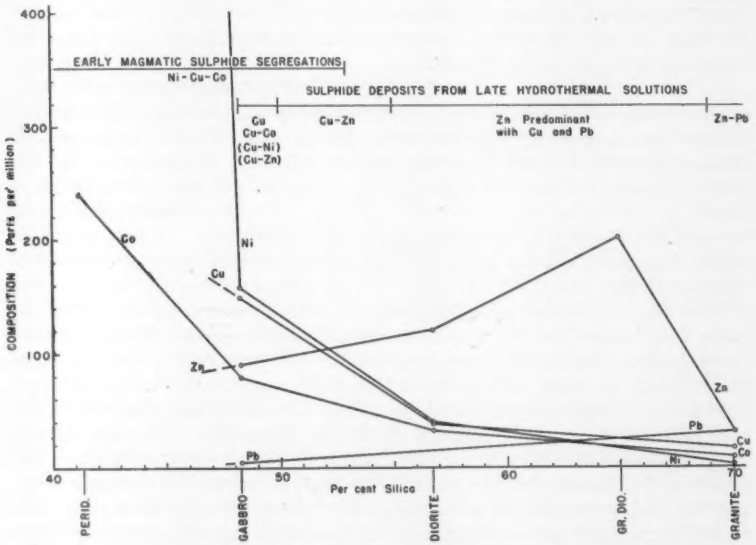


FIG. 4. Silica variation diagram showing nickel, copper, cobalt, zinc, and lead content of igneous rocks. Graphs are plotted from data in Table II using average silica content of the rock types calculated from Daly's analyses (11). The present figure is not final because more complete data will alter the graphs somewhat. For example, Lundegårdh's value for nickel in basic igneous rocks is lower than his value for zinc and is thus a figure that seems more probable from a study of the ore deposits. Final graphs must also have each analysis directly related to the silica in the analyzed rock.

geological map of the Sudbury district shows that the major contact ore bodies of the south range occur at Crean Hill, Creighton, Copper Cliff, Murray, and Garson, at each place where there is a downward bulge in the norite. In areas between these mines where the contact bulges upwards the contact is relatively barren of sulphide. The largest downward bulge is at Creighton where the largest of the contact mines occurs. The Frood orebody on the Frood offset is the greatest of all ore bodies at Sudbury for its depth. For many years it was considered too low grade to be ore until deep drilling proved

the increasing value at depth. It is now known that the offset in the Frood portion bottoms at about 2,800 feet below surface [5] and that the massive sulphides are concentrated at and near this bottoming of the norite rock. Similar conditions exist in other nickeliferous intrusions. In the Potgietersrust section of the Bushveld complex the copper-nickel sulphides occur at the base of the intrusive in marked downward embayments on the intrusive. At the Gap mine in Pennsylvania the sulphides occur in a pod at the center of the bottom of an intrusive basin. The typical pattern of concentration in downward embayments is almost everywhere apparent and in many of the mines follows this control in intimate detail.

Fault structure is of major importance in the location of some nickel ore bodies, in other nickel ore bodies faults are of no importance in the location of ore. Post ore faults of course may dislocate ore bodies at any mine but these are not being considered. At Creighton, Garson and Falconbridge much of the ore lies along fault structures but at Frood, Murray and Levack no evidence of major fault control has been found. Similarly with copper-nickel ore bodies outside the Sudbury district, faults may or may not be important in localizing the ore at the base of the intrusive. At Shebandowan the ore at the base of the intrusive is fault controlled but at Alexo, Ontario, and Rice Island, Manitoba, the ore lies at the base of the intrusive with no evidence of fault control.

The fault control of nickel-copper ore bodies is also peculiar in that the faults only control the ore in the immediate vicinity of the lower contact of the intrusive. As a fault passes into the footwall, the ore stops within a few hundred feet at most, and usually within a few tens of feet. Also where a fault passes upwards into the basic intrusive rock away from the contact, the ore terminates almost as abruptly as in the wallrocks. Not only do the sulphides end as ore, they actually disappear completely from the fault. It is apparent that nickel ore like chromite ore can be controlled by fault structure but both ore types were obviously not highly mobile at the time of their formation as they are not transported far from their parent intrusive or from their embayment locus even along faults which control the ore at its actual emplacement.

Wallrock alteration so common in most hydrothermal deposits is not consistent in copper-nickel sulphide bodies. In many mines or portions of mines fresh unaltered hypersthene in norite occurs as gangue of disseminated sulphide blebs or as fragments in massive ore. In other places uralitization is common and in a few mines such as Garson and Falconbridge in the Sudbury district, silica is abundant along some of the faults. As large or larger portions of fresh hypersthene-bearing norite occur in the immediate vicinity of the ore at Sudbury as in the remainder of the intrusion. In spite of considerable search no alteration aureoles have been found around the Sudbury ore bodies unless it be the copper-nickel sulphide dissemination itself.

Textures in the ore may give some evidence of the origin of the ore. In places sulphide stringers occur in fractures whose walls would fit back together

[5] Can. Min. Jour. 1946.

if the sulphide were removed. In other places replacement of fragments and wallrocks is apparent. The idea seems to be prevalent that replacement means hydrothermal solutions but liquid sulphide solutions in the smelter progressively replace (as well as dissolve) the most resistant bricks that can be devised so that it is apparent that pseudomorphous replacement by sulphide solutions is just as active and probably far more active than that by dilute hydrothermal solutions.

In places sulphides occur along cleavages of uralite. This has often been interpreted as sulphides added to the rock after uralitization but the texture may as readily be interpreted as a metamorphic texture due to the recrystallization of the silicate minerals and consequent rearrangement of enclosed sulphides by the relative forces of crystallization. The lack of crystal faces of sulphide in metamorphic rocks is ample evidence of the low force of crystallization or form energy of sulphide crystals. In fact the metamorphic origin of this texture is indicated in many specimens where sulphides occur along cleavage planes of the recrystallized uralite but not along the cleavage planes of the primary hypersthene, i.e., a redistribution of sulphides has taken place during recrystallization.

Vogt (34) has pointed out that some relationship exists between the size of a nickel-copper sulphide deposit and the size of the intrusion. He found that the larger Norwegian ore deposits occur with the larger intrusive bodies and the small ore deposits with the small norite bodies. This relationship holds for most copper-nickel deposits elsewhere but in exceptional areas large ore bodies, such as that at Petsamo, occur with intrusives only three or four times their own size. From our knowledge of sulphide solubility in silicate magmas it appears impossible that these sulphides could have segregated in place from the small amount of silicate magma. They must therefore have been injected as molten sulphides or deposited hydrothermally.

Nickel sulphide ore bodies are more often found associated with norites than with peridotites although the peridotites in general appear to be more common than norites. The solubility of sulphur decreases in more acid rocks (Fig. 5), so one possible explanation for the small number of sulphide ore bodies related to peridotites is that most peridotite magmas are undersaturated with sulphur and the sulphide separates out too late to allow accumulation by settling. This possibility is supported in the field by certain bodies such as the Ospwagan Lake, Manitoba, peridotite which consistently carries about 0.25% Ni. The nickel occurs mainly as sulphides spread more or less uniformly throughout the intrusive but it also occurs in the silicates as shown by assays of material from which the sulphide was leached. It appears that the sulphide content of the magma was so low that all the nickel was not extracted from the silicate magma and that the fine-grained sulphide separated when the silicate was largely crystalline and hence the sulphide could not aggregate to form sulphide ore bodies.

Nickel silicate ore bodies form as residual concentrations or are enriched below weathering zones on high-nickel peridotites. It is difficult to obtain fresh material from most of these intrusions but analyses indicate that such peridotites contain about 0.25% Ni and sulphur of the order of 0.01 percent

or less. Apparently the magmas contained so little sulphur that the nickel remained in the silicate form and as it is spread uniformly through the unweathered rock it is available for concentration during lateritic weathering.

Small veinlets of copper-nickel sulphides occur with pyrrhotite in certain granite and sedimentary gneiss areas where basic rocks are not found in the immediate vicinity of the sulphides. Thus far, however, sulphide veins found occurring in this manner are never more than a few feet long and a few feet wide.

Nickel also occurs in a few of the copper-zinc replacement ore bodies where occasional assays may show as much as 0.5% Ni but the nickel content is not consistent as it is in the copper-nickel ore bodies.

Summarizing the occurrence of nickel deposits, it is apparent that nickel deposits, like chromite deposits, are related to igneous intrusions of a particular composition. The nickel deposits are related to the high magnesia rocks as

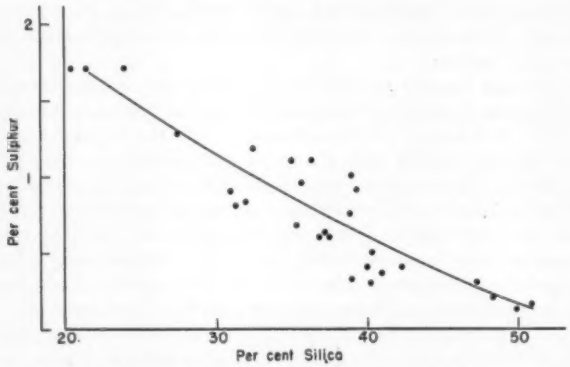


FIG. 5. Silica variation diagram showing sulphur solubility in silicate melts. Plotted from Vogt's data (33). Note that this is "dissolved sulphur" as distinguished from "suspended sulphur" in sulphide droplets.

would be expected from the size and charge of the ions. Nickel deposits like chromite deposits are found in particular portions of intrusive bodies and although both show some mobility during their formation, that mobility is limited and the deposits remain within or very close to the related intrusive.

SULPHUR.

Sulphur is discussed at this point because of the transitional character of the ore deposits of the elements with ionic radius slightly greater than nickel. Nickel characteristically occurs in the sulphides at the base of associated basic intrusives. The somewhat larger copper and cobalt ions occur both with nickel deposits and in the typical hydrothermal replacement deposits that are not directly related in space to any particular intrusive. The still larger zinc and lead ions occur largely in typical hydrothermal deposits. It is be-

lieved that sulphur plays an important role in determining the character of these ore deposits.

The distribution of sulphur in igneous rocks is complex because sulphur may separate as an immiscible liquid in the early magmatic stage or it may exist in volatile forms in the late magmatic stage. Solubility of sulphur in rocks or magmas is also difficult to determine as both dissolved and suspended sulphides must be considered. However the available analytical data combined with microscopic data and field evidence provide enough information to arrive at a reasonable theory of the probable role of sulphur in ore deposition.

Vogt (33) determined the sulphur solubility in slags considering dissolved and suspended sulphides separately. Vogt's results are plotted in Figures 5 and 6. Slags are not completely analogous to natural magmas as they are

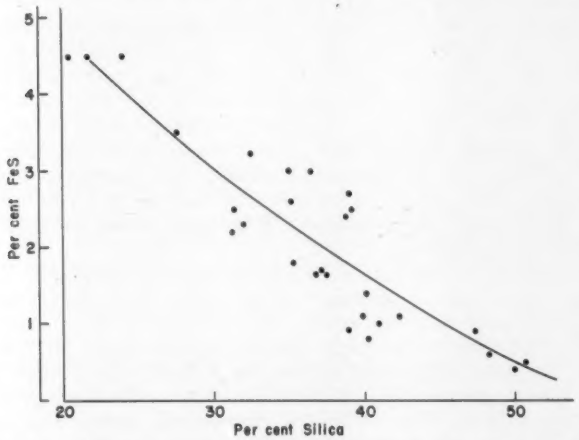


FIG. 6. Silica variation diagram showing solubility of troilite in silicate melts. Plotted from Vogt's data (33).

mostly higher in iron and lower in magnesium, however, it is common practice to decrease sulphide solubility in slag of any composition by adding silica. It is apparent from the spread of the points in Figures 5 and 6, that sulphide solubility differs in slags of different composition but all follow the same tendency of lower sulphide solubility with higher silica. It is probable, therefore, that sulphur solubility decreases with increasing silica content of magmas and that the relative solubility in magma is similar to that in slag. Thus, magmas with more than 55 per cent silica must have a very small dissolved sulphur content, whereas magmas with less than 55 percent silica may carry considerable sulphide in solution (Fig. 5). Figure 5 also shows that sulphur solubility increases very rapidly in slags (or magmas) carrying less than 50 percent silica. Therefore large amounts of sulphide should separate as a magma fractionally crystallized, and the rest liquid changed from say 40%

to 50% SiO_2, yet the amount of silicate crystallization may not be very great. A granitic magma however apparently cannot carry much sulphide in solution and the change in sulphide solubility must be very slow during crystallization. Thus, a logical conclusion from Figures 5 and 6 appears to be that considerable sulphide may separate during crystallization of a basic magma, but it is unlikely that a sulphide segregation can accumulate from an acid magma because the acid magma can contain so little sulphide in solution, and because the rate of change of sulphide solubility with changing magma composition is so slow. The viscosity of high silicate melts must also hinder sulphide segregation.

Newhouse (20) concluded from a microscopic study of sulphides in igneous rocks that femic rocks have more sulphides and hence have a higher "solubility" of sulphides than salic rocks, thus indicating that sulphide solubility in natural rocks is similar to that of slags.

A study of the field distribution of sulphide bodies shows that many igneous intrusives having the composition of gabbro, norite, pyroxenite, and peridotite have sulphide bodies associated with them, and the composition of the sulphides is related to the igneous silicate body. The sulphide bodies occur either within or even more commonly at the base of the intrusive where gravity is a probable concentration factor. Rocks as salic as diorites very rarely have similar but small associated sulphide concentrations. The author is not aware of any example of a sulphide at the base of a salic igneous intrusion. It is obvious therefore that sulphide segregations are related to the femic rocks and not to the salic.

The conclusion is therefore reached that sulphides segregate by liquid immiscibility from a basic or ultrabasic magma during fractional crystallization. This magmatic sulphide is apparently enriched in the thiophile elements concentrated in the basic and ultrabasic silicate magmas, that is Ni, Cu, and Co (Fig. 4). As intermediate and acid magmas cannot contain much dissolved sulphide, liquid sulphide segregations cannot form, so no corresponding sulphide segregations are found enriched in the elements, such as lead, which are concentrated in late magmatic crystals or liquids.

COPPER.

Geochemistry.—The ionic radius of Cu^{2+} was only approximately known until recently. Rankama and Sahama (24) give the radius as approximately equal to that of Fe^{2+} (0.83 Å). Ahrens (1) using ionic potentials and a different radius for O^{2-} (1.40 Å) from that in Rankama and Sahama's table (1.32 Å) has determined the hitherto unknown radius of Cu^{2+} as 0.72 Å the same as the radius of Co^{2+}. Therefore to make the value of Cu^{2+} comparable to the value for the other elements in Rankama and Sahama's table, Cu^{2+} is taken as being 0.82 Å, the same as Co^{2+}. In Ahrens table, both Co^{2+} and Cu^{2+} are 0.02 Å smaller than Fe^{2+}. The distribution of copper should therefore be similar to that of iron, with copper concentrated somewhat more towards the basic end of a differentiated rock series.

Distribution in Igneous Rocks.—Wager and Mitchell (36) have determined the distribution of copper in the silicate rocks and minerals of the

differentiated Skaergaard intrusive. They found that copper "is strikingly more abundant in the later middle part of the series than in either the earlier or latest rocks." They have also shown that copper was at a maximum in the magmatic liquid in the same part of the series. Sandell and Goldich (26) determined the copper content of rocks as follows:

Rock type	% Cu	% SiO_2
15 basic rocks	0.0149	48.5
11 intermediate rocks	0.0038	62.0
20 silicic rocks	0.0016	72.0

The distribution of copper is close to that expected from the ionic radius.

The copper in igneous rocks has usually been observed to be most abundantly present in the form of sulphides, although apparently it may also be concentrated in the silicate minerals as indicated by Wager and Mitchell (36). Copper is a thiophile element and, as it is one of the minor elements of the magma, the great proportion of copper would be expected in the sulphides in magmas where sulphide is available. Newhouse (20) showed that magmatic sulphides were present in all the gabbros that he examined; hence it appears that in most magmas sulphur is available for the copper in the basic magmatic stage when copper is most concentrated in the magma. The availability of sulphide in a basic magma is also suggested by the solubility curve of sulphur in slags (Fig. 5). Basic magmas are in the position on the curve where appreciable quantities of a sulphide liquid could still be separating from a silicate liquid as composition changes to more silicic, yet total solubility of sulphur is low enough that apparently most magmas are saturated with sulphur at this stage.

Copper Ore Bodies.—Copper ore bodies occur in two distinct associations that must be of genetic significance. Copper occurs with nickel and cobalt in sulphide ores that are related both in space and composition to associated intrusive masses. It also occurs alone, or with zinc, or zinc and lead in large replacement ore bodies with hydrothermal associations. It is usually not possible to relate this latter type of ore body to any particular intrusive by direct association in space; thus the material must have travelled considerable distance from its source. Copper ores may also occur as a sedimentary or secondary type of ore body but these are not being considered here. Considering the distribution of copper in igneous rocks from basic to acid members, the two types of ore bodies, and the solubility of sulphides in silicate magmas, it seems logical to conclude, first, that the copper-nickel sulphide ore bodies are formed from basic and ultrabasic magmas at an early stage while sulphide is unmixing from the silicate liquid during fractional crystallization, and second, that once sulphide is no longer segregating in appreciable amounts from the intermediate and acid magmas only hydrothermal ores of copper, zinc and lead can separate at the end stage of crystallization when water becomes concentrated enough to escape from the magma and concentrate and transport the hydrothermal sulphides to the regions where they are finally deposited.

The distribution of the copper in the sulphide of the copper-nickel sulphide ores is significant. As already stated the amount of nickel in the

sulphide decreases as the associated rock changes in composition from ultrabasic to basic. Vogt (34) has shown the copper content does not decrease in the sulphides in proportion to nickel, but that if anything increases slightly in the sulphides associated with basic rocks. A similar observation may be made concerning Canadian copper-nickel deposits. The behaviour of the sulphide ore bodies therefore corresponds to the trace element distribution in igneous rocks.

COBALT.

Geochemistry.—The ionic radius of Co^{2+} is 0.82 Å. It is thus slightly smaller than Fe^{2+}, the nearest of the major ions to cobalt in size. The radii of Co^{2+} and Cu^{2+} are very similar and according to Ahrens (1) they are identical. Cobalt, like copper, is thiophile. It may be expected therefore that cobalt and copper distributions may be similar.

Distribution in Rocks.—The distribution of cobalt in silicate rocks bears similarities to both copper and nickel. Like nickel, cobalt appears to decrease in amount progressively from ultrabasic to granite rocks; the rate of decrease of cobalt, however, is very much less than that of nickel. In the basic, intermediate and acid rocks the distribution of cobalt is actually closer to that of copper than to that of nickel (Table II and Fig. 4).

Cobalt in Ore Bodies.—The occurrence of cobalt in ore bodies is more nearly like that of copper than nickel. Cobalt occurs in large amounts in both copper-nickel sulphide ore bodies directly associated with basic intrusives, and in copper ore bodies with hydrothermal associations. Cobalt also occurs to a minor extent in arsenical ores that may also contain copper and nickel.

In recent years the greatest cobalt production has come from the copper-cobalt ores of the Congo and Rhodesia.[6] This production will soon be augmented by the copper-cobalt ores of the Kilembe mine in Uganda, the Blackbird mine in Idaho, and possibly the copper-cobalt ores of the Coldstream mine in Canada.

Large amounts of cobalt are also contained in the copper-nickel sulphide ore bodies, although until recently most of this cobalt has been lost in the smelting and refining operations. Data on the distribution of cobalt in these ores are not yet complete but some tendencies show that it is more like copper than nickel in its distribution. Analyses of ores from the Erteli, Meinkjar-Nysten and Beiern mines in Norway (4) indicate that the copper: cobalt ratio is much more constant than the nickel: cobalt ratio.

The cobalt arsenide association with quartz diabase is well known in the Cobalt region and elsewhere in Canada. It is difficult to find analyses of the ores in the literature, but Knight (16) states that cobalt, nickel, copper and arsenic are byproduct metals of the silver ores at Cobalt. Collins (9) discussing the cobalt silver ores of the Gowganda area, Canada, states (p. 102): "the ore minerals form a characteristic group of native metals, sulphides, arsenides and related compounds of cobalt, nickel, silver, and copper," and (p. 103) "chalcopyrite is more abundant than any of the other (ore) minerals,

[6] Two-thirds of total in 1937—Minerals Yearbook.

but this fact is obscured by its inferior commercial value." At Werner Lake Ontario, the cobalt ores are composed principally of cobaltite and chalcopyrite mixed with gangue minerals. Nickel is rare in the Werner Lake ores. These copper-nickel-cobalt-arsenide ores are closely associated with quartz diabases in Canada and the veins have hydrothermal characteristics.

ZINC.

Geochemistry.—The ionic radius of Zn^{2+} is 0.83 Å, the same as that of Fe^{2+}; hence the distribution of zinc should be somewhat similar to that of iron. Zinc like iron is thiophile but as it is only a minor element it may be largely concentrated in sulphide minerals. The geology of the zinc ore deposits indicates that zinc is greatly concentrated in certain hydrothermal types of deposit. It appears therefore that if a hydrothermal phase forms, zinc goes into the hydrothermal phase in preference to the silicate phase.

Zinc in Silicate Rocks.—The distribution of zinc in silicate rocks is still contradictory to some extent. Sandell and Goldich (26) determined that zinc is concentrated in basic rocks compared to acid rocks in the ratio of approximately 2:1. Lundegårdh (17) however found that zinc was most concentrated in granodiorites with lesser amounts in both gabbros and granites, Lundegårdh's figures are used in Table II and Figure 4, as his data with respect to rock types are more complete. He stated that the distribution of zinc was parallel to that of biotite. The distribution of zinc is somewhat analogous to that of iron although the concentration peak appears more towards the salic end of the igneous rock series. Newhouse (20) did not find sphalerite in igneous rocks. Neumann (19) has given a crystal chemical explanation for the distribution of zinc but the geological factors governing extraction of minor elements, such as zinc, in sulphide or hydrothermal phases may be of even more importance. Only small proportions of a major thiophile element such as iron may be extracted in sulphide or hydrothermal phases but very large proportions of the minor elements may be removed from silicate magmas before final consolidation of the silicates. Thus the majority of iron remains in the silicate minerals, but the greater part of the zinc does not, so that the geochemistry of zinc and iron do not correspond exactly.

Ore Deposits of Zinc.—Most of the major ore deposits of zinc are the hydrothermal replacement type which needs little explanation as their characteristics are so well known. The zinc in these deposits may be associated with copper or lead.

Zinc also occurs to some extent in the copper-nickel deposits but the relative concentration is much less than that of nickel and copper. Noddack and Noddack (22) determined that an average of 57 magmatic sulphides contained 0.85% Zn, 1.09% Cu, and 3.14% Ni. This amount of zinc is undoubtedly too high for the Canadian copper-nickel deposits, although in some copper-nickel ores zinc may be an important element. The analyses of Noddack and Noddack do indicate that a significant proportion of zinc does enter this type of deposit, although data concerning the relation of zinc to rock type in these deposits are still incomplete.

LEAD.

Geochemistry.—The ionic radius of Pb^{2+} is 1.32 Å. This value closely corresponds to that of K^{1+}. Lead might therefore be expected to concentrate with early potash feldspar crystals as lead has a slightly smaller ionic radius and has double the valence of potassium. Lead has also been found to partly replace Ca^{2+} in some silicate minerals. Lead is a thiophile element and like zinc it is obviously highly concentrated in the hydrothermal type of deposit.

Occurrence in Igneous Rocks.—Lead is concentrated in the acid igneous rocks. Sandell and Goldich (26) found that the silicic rocks they analyzed contained about twice as much lead as basic rocks. Hevesy, Hobbie and Holmes (15) found that granitic rocks contained six times as much lead as gabbros and related types. The results of Hevesy, Hobbie and Holmes are shown in Table II and Figure 4.

Lead Ore Deposits.—Lead commonly occurs in hydrothermal deposits with zinc and may also occur with copper and silver. Many of these deposits are associated with granitic rock.

Newhouse (20) was unable to find a lead sulphide mineral as a minor constituent of igneous rocks. Noddack and Noddack (22) found only 0.001% Pb in the fifty-seven magmatic sulphides they analyzed, showing that lead is almost non-existent in these ores associated with the basic rocks.

THE COPPER-ZINC-LEAD DEPOSITS.

Sandell and Goldich (26) have determined the distribution of the minor elements Cu, Zn, and Pb in silicate rocks. They found that these elements "may be divided into three major groups": (1) a copper-zinc group chiefly in rocks ranging from 47–60 percent silica, with copper predominant in the lower silica range; (2) a zinc group with zinc clearly predominant and almost equal proportions of copper and lead, this group occurring in samples ranging from 60–75 percent silica; (3) a zinc-lead group in highly siliceous igneous rocks generally containing 73 percent or more silica.

A study of the Canadian copper, zinc, and lead deposits shows that the ore deposits occur in a similar grouping of copper deposits; copper-zinc deposits; zinc deposits with some lead and copper; and zinc-lead deposits (Table VI). The similarity of occurrence of these elements in ore deposits and in igneous rocks is most suggestive of a genetic relationship.

It is now becoming well known that the base metal ore deposits in Canada occur in groups, and that these groups have a certain constancy in composition. For example, in the Flin Flon district the Flin Flon, Mandy, Cuprus, and Schist lake mines and several smaller prospects are all copper-zinc mines. Other mineral types such as lead-zinc or lead-silver deposits do not occur near Flin Flon. These groups are not examples of zoning, they are deposits throughout the whole district which form a characteristic group such as occurs in the igneous rocks themselves. The same type of distribution occurs in other districts. A group of copper and copper-zinc mines occur in the Noranda district; zinc deposits with lesser amounts of copper and lead occur in the Sudbury basin; other districts are known lead-zinc districts. It is ap-

parent therefore that different districts have characteristic ore types and just as apparent that these ore types are concentrated in specific limited districts in spite of the favorable structures and channelways that may continue beyond the limits of ore mineralization or may occur where there is no ore mineralization of any kind.

It is usually difficult to determine the magma or specific intrusive from which hydrothermal deposits of copper, zinc, or lead have originated as the metals have travelled considerable distances from their source and the final emplacement of the ore appears to be controlled largely by structural, physical

TABLE VI.

TYPES OF COPPER-ZINC-LEAD DEPOSITS.

Type	Locality	Grade of ore		
		% Cu	% Zn	% Pb
Copper	Noranda	7.05		
Copper-zinc	Flin Flon	1.44	2.23	
	Cuprus	3.62	6.8	
	Mandy			
	Schist Lake			
	Normetal	3.32	7.59	
	Quemont	1.43	2.87	
	East Sullivan	1.78	0.87	
	Waite Amulet			
	East Waite	4.0	3.0	
	C Shaft	1.8	1.3	
	Lower A	5.76	4.08	
	Upper A	1.11	6.02	
	Ore below 1,000′	2.75	0.6	
Zinc predominant	Golden Manitou	.06	7.18	.82 calc.
	Macdonald		3.5	
	Treadwell Yukon*	1.05	4.55	1.00
Lead-zinc	Consolidated (Sullivan)**		5.93	6.35
	Highland Bell			
	(calc. from production)		2.96	2.16
	New Calumet		7.7	2.4
	Pine Point, N.W.T.		7.0	9.0
	Silback Premier		2.6	2.2

Source: Canadian Mines Handbook (1951), figures on ore reserves, or production for a year.

* Figures from Ont. Dept. Mines, 39th Ann. Rept., Pt. 1, 1930.

** Includes some custom ore.

and chemical conditions. However, a glance at the geological map of Manitoba (G.S.C. 850 A), Saskatchewan (G.S.C. 895 A), and Southern Quebec (G.S.C. 703 A) shows the spectacular concentration of numerous basic and intermediate intrusives in the immediate vicinity of the Flin Flon and Noranda copper-zinc districts and the scarcity of such intrusives in areas that might otherwise be considered favorable (Figs. 7, 8). In the British Columbia districts where lead-zinc deposits are common, the intrusive rocks are acidic (G.S.C. map 820 A). These relationships of intrusive distribution to ore type appear more than coincidental when the distribution of the elements in

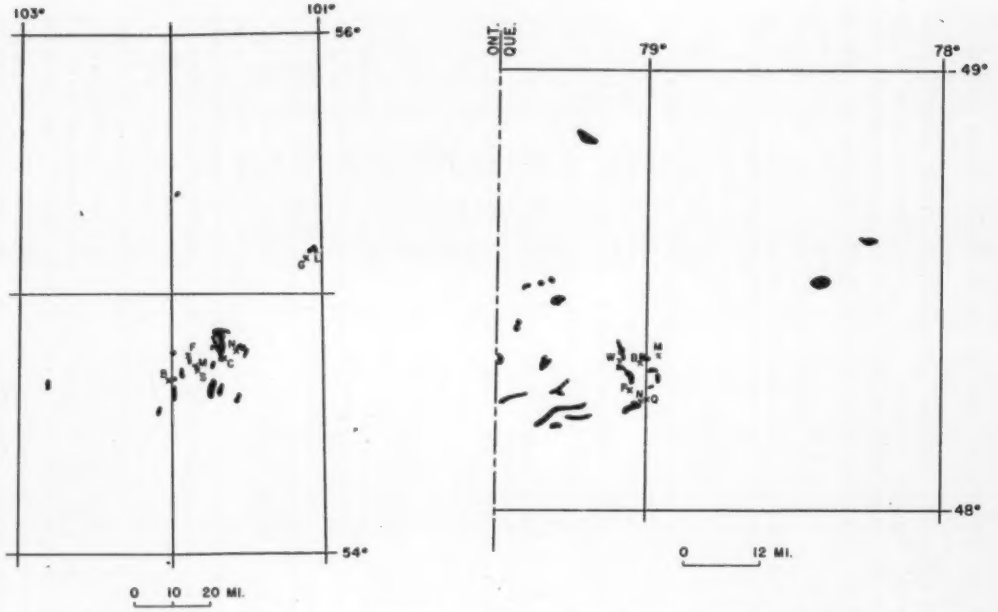


FIG. 7. The distribution of copper-zinc ore deposits, relative to the group of intrusions included in the legend as quartz diorite, diorite, quartz gabbro, and gabbro in the Flin Flon area. Adapted from G. S. C. maps 850 A—Manitoba and 895 A—Saskatchewan. All basic intrusives shown on the maps are shown on the figure. The ore deposits are: B—Birch Lake, C—Cuprus, F—Flin Flon, G—Sherritt Gordon, L—Bob's Lake, M—Mandy, N—North Star, S—Schist Lake.

FIG. 8. The distribution of ore deposits and prospects relative to the group of inclusions included in the legend as quartz diorite, diorite, and gabbro in the Noranda area. Adapted from G. S. C. map 703 A—Southern Quebec, West sheet. B—Newbeck, M—Macdonald, N—Noranda, P—Pontiac Rouyn, Q—Quemont, W—Waite Amulet.

the igneous rocks and the fundamental geochemical laws governing distribution of the elements are considered.

The ore deposits of the Sudbury district are of interest when considering the distribution of the elements in districts. The distribution of the copper-nickel deposits around the base of the Sudbury intrusion is well known and has already been mentioned in this paper. Much less has been written about the copper-zinc-lead mineralization of the Sudbury district, yet it is of major proportions and is currently undergoing intensive exploration and development in preparation for production. The copper-lead-zinc ores which are

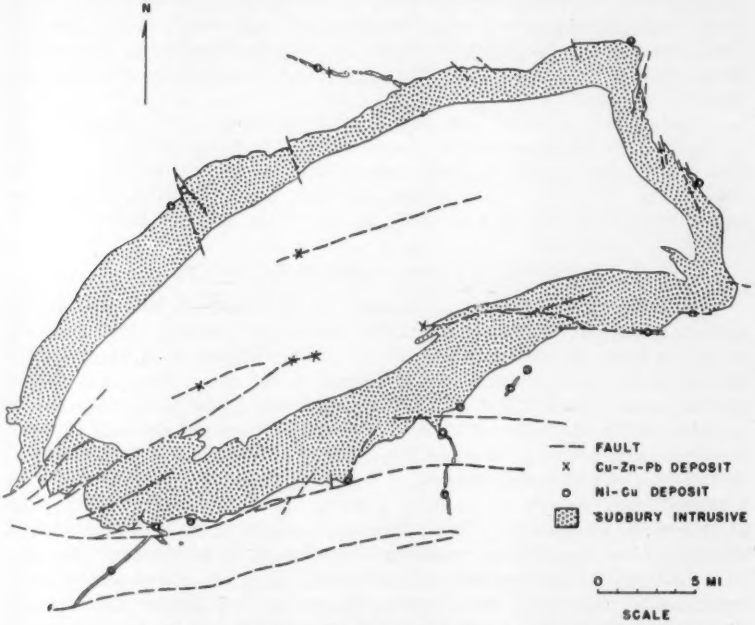


FIG. 9. Distribution of copper-nickel and zinc-copper-lead deposits in the Sudbury District, Ontario.

of the predominant zinc type (Treadwell—Yukon, Table VI) occur along faults within the Sudbury basin, that is structurally above the micropegmatite (Fig. 9). This mineralization occurs along several of the faults over a strike length of several miles, and along faults several miles apart, yet always within the basin defined by the Sudbury intrusive. The same faults have been traced through the intrusive and beyond the lower contact of the intrusive for many miles, yet in spite of the intensive field mapping and excellent exposures, the copper-zinc-lead mineralization has not been found beyond the outer limits of the micropegmatite. The widespread mineralization thus oc-

curs only in the basin, structurally above the micropegmatite where no other intrusive is found. It is highly probable therefore that if these are hydrothermal ores, they came from a hydrothermal phase of the Sudbury intrusion.

The Sudbury micropegmatite has an average silica content of 67.8 percent (10). It may be seen from Figure 4 that the expected ratio of Cu : Zn : Pb in a rock containing 67.8 percent SiO_2 is 1.0 : 5.2 : 1.4. The actual ratio of these elements in the Treadwell-Yukon mine, the largest of the ore bodies is 1.05 : 4.55 : 1.00. This close agreement is probably fortuitous as the graphs in Figure 4 are only first approximations and the Treadwell Yukon ore may not have the exact composition of the average ore in the district. However, taken in conjunction with the geological occurrence of the ores and their geographical relation with respect to the micropegmatite, the relative proportions of the elements are very suggestive of a genetic association of the ores with the igneous rock types.

It might also be noted that the Garson copper-nickel ore bodies occur at the base of the intrusive partially localized along branches of the same faults that control the Treadwell Yukon copper-zinc-lead ore at the center of the basin (Fig. 9). Both types of ore, therefore, appear related to the same period of fault activity and probably to the whole Sudbury basin intrusive period.

ZONING AND PARAGENESIS IN ORE BODIES.

The deep-seated Canadian ore deposits occur in districts having relatively uniform groups of deposits of the major base-metal types with little evidence of zoning either in individual deposits or in the districts as a whole. This type of major zoning which may be related to the composition of a parent magma should be clearly distinguished from the zoning and paragenesis shown by many of the shallower or lower temperature base-metal deposits of other countries, where zoning occurs within a single ore body or within a district. In this type of zoning the minerals of the different elements are deposited in a characteristic succession, possibly grading outwards from a central area as at Butte and Cornwall. This zoning and paragenesis have been discussed extensively and need not be considered here except as an accepted observation. The zoning and paragenesis have usually been considered to be due to a decrease in solubility of the elements that results from gradually decreasing temperature and pressure, or changing chemical conditions as solutions travel away from their source. These conclusions are reasonable; they are well supported by facts and generally accepted. It is of interest to compare this zoning and solubility with the structure of the sulphide minerals.

The bond type of sulphide minerals differs from that of the silicates. In silicates, the bonding is essentially of the ionic type. In common sulphide ore minerals the bonding is more nearly homopolar (or covalent) with some of the bonds grading to metallic or other types.

Bateman (3, p. 107) states that "the same order of deposition (of ore minerals) is repeated in numerous localities the world over," and that the general sequence is "iron sulphides or arsenides, sphalerite, enargite, chalcopyrite, bornite, galena, gold, and complex silver minerals." In order of deposition the elements then are Fe, Zn, Cu, Pb, Au, and Ag. It is appar-

ent from Table VII that this is in the order of the increasing size of the octahedral and tetrahedral radii of these elements. The radii of Bi and Hg are also included in the table as they are notably late minerals.

THEORY OF ORE DEPOSITS.

At this stage a working hypothesis for the origin of ore deposits may be outlined briefly. The whole problem is treated according to what might happen if a parent magma, say of basaltic composition, differentiated completely starting with the production of ultrabasic members and ending with the final consolidation of the pegmatitic and hydrothermal material. It should be remembered, however, that a particular magma may start with any initial composition and may crystallize with little differentiation and expel its hydrothermal constituents, but each intrusion with its related ore products should in general fit into its place in the generalized scheme according to its composition. Nockolds and Mitchell (21) have shown that trace elements have the same type of variation whether in a layered lopolithic intrusive such as the Skaergaard, or in an intrusive complex of separate but genetically related intrusives such as the Caledonian plutonic rocks.

TABLE VII.

TETRAHEDRAL RADII OF THE ELEMENTS.

*Fe^{II}	1.23 Å
Zn	1.31
Cu	1.35
Pb	1.46
Bi	1.46
Hg	1.48
Au	1.50
Ag	1.53

* Octahedral radius.

Source: Wells (39), p. 50 and 51.

If we assume the formation of a magma involves the melting of crystalline rocks the melting is more or less the opposite of crystallization depending upon fluxing conditions. Acid minerals melt early and the liquid may be removed at any stage depending upon geological conditions. Magma formation therefore involves separation or concentration of the major elements and their accompanying minor camouflaged or captured elements. Thus individual magmas may begin their crystallization with certain elements already concentrated depending upon the history of formation of the magma.

As a magma crystallizes fractionally the minor elements are concentrated along with the major elements according to Goldschmidt's principles of ionic radius and valency. However, three possibilities for further concentration of particular elements exist: (1) the formation of an immiscible sulphide liquid phase during the early stage of crystallization; (2) the formation of a hydrothermal phase by boiling during late stages of crystallization, and (3) the formation of a final silicate or pegmatitic stage in which are concentrated the elements of lithophile character which preferentially stay in the silicate

phase and which are of too unsuitable ionic radius or valency to be concentrated with any of the major elements.

Oxide crystals may be formed during the early stages of crystallization possibly under such conditions as described by Bowen (5) or from a late magmatic liquid, which appears necessary to fit the field facts as described by Bateman (3a). The composition of these oxide minerals depends upon the stage of differentiation with the smaller ions of aluminum, chromium and magnesium concentrated in the earliest crystals associated with peridotites; and the larger ions of iron, vanadium and titanium concentrated in later crystals associated with gabbros.

A sulphide liquid may separate from the silicate liquid at any time depending upon initial sulphur concentration in the magma. If sulphur is highly concentrated, the separation of a sulphide liquid may take place due to falling temperature before crystallization begins if the magma contained any superheat, and separation would continue throughout the crystallization. In magmas with low sulphur concentration, sulphide separation may begin after crystallization has started as the initial magma was not saturated with sulphide. Early silicate crystals may therefore contain camouflaged thiophile elements if they have been separated before a sulphide liquid formed.

A sulphide liquid has a higher gravity than a silicate liquid or liquid-crystal mush, hence it would be expected that a sulphide liquid would tend to collect at the base of the magma from which it was separated.

The sulphide liquid has a lower melting point than the silicates or silicate mixtures of the basic and ultrabasic igneous rocks as shown by both known melting points and the textures in igneous rocks (e.g., Newhouse—20). Thus, in a basic intrusion sulphide is still liquid when the silicate portion is solid or almost solid, and the sulphides may be moved along fractures in the direction of relief of pressure. The sulphides, however, are close to their freezing point and do not travel far from the parent intrusive as they are so quickly chilled by the wallrocks. Thus, magmatic sulphides are always closely related to the parent intrusive and generally located at or near the base.

Sulphide segregations are not found with granitic rocks for two reasons: (1) sulphide solubility in granitic magma is extremely low, and (2) the temperature of crystallization of sulphide is apparently higher than that of the silicates as textures of granitic rocks show that sulphides crystallize early (20). Thus, there is no possibility of droplets sinking and coalescing beyond the very early stage of the crystallization period.

The composition of a sulphide liquid separating from a silicate magma depends upon the composition of the liquid silicate and any suspended crystals as it must be in equilibrium with these. However if a droplet of sulphide settles into a portion of the magma chamber where crystals are also settling or have previously settled, the liquid sulphide must tend to reach equilibrium with both the silicate liquid and early crystals in the settling area. The composition of the sulphide therefore will correspond to the rock with which it is associated as equilibrium is apparently generally approached. Thus, if early silicate crystals extracted nickel from the magma, the thiophile nickel may

pass from the silicate crystal to the newly arrived sulphide liquid until equilibrium is reached. This actually happens under laboratory conditions.

The nickel : sulphur ratio in the ore is therefore related to the composition of the rock. Copper on the other hand is not concentrated in early crystals, so copper and nickel vary independently. A slightly higher copper : sulphur ratio might be expected in sulphides associated with gabbro than with peridotite and this appears to be the general case, although initial concentration differences of copper in different magmas may give high copper in some ore bodies associated with very basic rocks. Zinc may enter the magmatic sulphides to some extent but zinc reaches its maximum concentration in the magma at a much later stage than the formation of the magmatic sulphides. Lead is concentrated still later and is not an important element in magmatic deposits even though it is thiophile. The relative thiophile character of the elements must also be considered though the concentration appears to be the most important factor.

In the late stage of magma consolidation water apparently becomes more concentrated and in the last residual stage the magmatic liquid appears to separate into two phases: (1) a silicate phase containing considerable water and the minor lithophile elements not related to the major elements in ionic size or charge, and (2) a tenuous "hydrothermal" phase containing the metallic elements whose ions are in general the thiophile types. The silicate phase is represented by the pegmatite dikes, which in many places show evidence of forceful intrusion and fractional crystallization, and contain concentrations of the rare lithophile elements.

The hydrothermal phase carries the elements away from the source magma and they are subsequently deposited in vein and replacement deposits. The chemical composition of these solutions depends to a large extent on the composition of the intrusive body in which they originate. If the solutions are residuals from basic to intermediate magma, then copper or copper-zinc ores predominate; if from an intermediate magma, then zinc predominates; if from acid magma, then lead-zinc is dominant. It is not impossible for nickel to be in part hydrothermal but it appears that the major portion of the nickel is extracted as magmatic sulphides and that the amount of hydrothermal material from the very basic rocks is not large.

Individual hydrothermal deposits may also be zoned or show a regular paragenetic relationship of the minerals because of the relative solubilities of the elements. These relative solubilities in turn show a marked relationship to the tetrahedral radii of the elements.

Geological and geochemical evidence appear to fit this generalized theory of origin of ore deposits. The distribution of the elements is controlled primarily by the structure of the ions or atoms—their size, their valence, and the configuration of their electron shell structures. The distribution, however, must be complicated by many geological factors such as different lines of descent from the magma according to pressure and temperature conditions; differing concentration of elements in the original magmas, particularly water and sulphur; state of oxidation of the system; difference in de-

gree of differentiation in large and small intrusives; and probably many other factors. The close dovetailing between the structure of the ions, geochemical laws, and the geological occurrence of ore bodies however create such a consistent pattern as to suggest that the present ideas of ore genesis are following the right path, and this gives confidence to use such knowledge in search for more ore.

EXPLORATION PRINCIPLES.

If the foregoing theory is accepted as a working hypothesis, then certain rules regarding exploration become apparent. It is realized that it may be necessary to modify the generalizations when further facts have been accumulated, and also that certain exceptions to the general rules may be found.

Chromium.—(1) Chromite has always been found in ultrabasic rocks and there is now the geochemical explanation as to why it occurs there and only there. Consequently, it would not be looked for elsewhere.

(2) The Cr_2O_3 content and the Cr : Fe ratio of chromite in a possible ore body can be established from a hand specimen or from any single outcrop of the deposit. The grade of ore will depend on the amount of silicate impurities but the composition of the chromite will remain relatively constant.

(3) In a layered intrusive the higher grade chromites tend to be located towards the base of an intrusive, the closer to the bottom the better the hope for commercial chromite. In an undifferentiated ultrabasic intrusive, however, the chromite is likely to be similar throughout the intrusive.

(4) Traces of Cr_2O_3 are not to be taken as "indicators" that better grade material will occur, but, on the contrary, that good grade chromite does not occur in that particular body.

(5) The progressive change in composition of oxide bands in layered intrusives such as the Bushveld, must mean that these oxide minerals are early magmatic and their composition corresponds to successively formed layers of silicate in the intrusive. The oxides in places may be transported for a short distance along fractures, but the amount of transport is limited and the chromite does not move appreciably through cold country rocks.

Vanadium.—(1) Vanadium is concentrated with titaniferous magnetite ores associated with norites and gabbros. Certain bands may contain large enough concentrations of vanadium to be seriously considered as a source of that element. The vanadium content should be consistent so a few assays should establish the position of the particular ore body having the greatest concentration.

(2) Because of its ionic radius and valence, it is probable that vanadium is camouflaged in the magnetite structure at high temperatures of crystallization. In most titaniferous magnetites, the vanadium seems to remain in the magnetite structure and cannot be concentrated by milling. However, it is possible that a vanadium mineral may form by exsolution during the cooling stage. An example of an iron vanadate mineral associated with magmatic ilmenite has been reported from Russia by C. de Leuchtenburg.[7] It was possible to concentrate this vanadium by milling.

[7] Personal communication.

Titanium.—(1) High-grade ilmenite ore deposits associated with igneous rocks are found only in anorthosites and gabbros and there is good reason to believe they will not be found elsewhere as primary deposits.

(2) As with chromite, the TiO_2 content and the Ti : Fe ratio of a deposit associated with a basic igneous rock may be established from one outcrop. If the Ti : Fe ratio is unsatisfactory it is unlikely to improve in that ore body, although it may be different for other ore bodies in the same intrusive complex.

(3) Magnetite bands or segregations occurring in gabbroic rocks will be titaniferous. The magnetite bands of most intrusives will contain too much titanium to be considered as iron ore by present smelting standards, but it is quite possible that rare magmas will be so low in original titanium that magnetite bands of low titanium content may form. It should not be difficult to establish the titanium distribution.

Nickel.—(1) Nickel sulphide ore bodies occur in association with basic and ultrabasic intrusive rocks only, either within or very close to the parent intrusive.

(2) Present day commercial grade nickel ores are all associated with norites or more basic rocks. The sulphides associated with gabbros and diorites do not contain enough nickel to be extracted by present day methods, although the nickel may be recovered as a by-product in the future if large enough sulphide bodies are found.

(3) The grade of nickel in the sulphide is related to the associated igneous rock, the more basic the rock the better the Ni : S ratio in the sulphide.

(4) As with chromite and ilmenite, the amount of nickel in the sulphide of the whole ore body, that is, the Ni : S ratio of the ore, can be determined from a single pit or even from hand specimens, provided the sulphides are not weathered or do not contain abnormal amounts of chalcopyrite. Low nickel content in a sulphide can be taken to indicate that ore-grade nickel deposits do not occur in that particular sulphide occurrence.

(5) The nickel sulphide ores always contain copper and cobalt, and zinc should also be determined as it may be a possible by-product or may interfere with the smelting.

(6) The nickel sulphides in the vast majority of deposits are concentrated at or near the base of the intrusive. The best primary structure is a trough in the bottom of the intrusive, but secondary fault structures may also serve to localize ore in the primary structure.

Copper.—(1) Copper ores should always be checked for cobalt because of the cobalt-copper association.

Copper-Zinc-Lead.—(1) Copper-zinc-lead ore bodies, or any combination of these elements in ores, occur as replacement deposits localized along structures at some distance from the parent intrusive. However, it is probable that they have a parent magma or intrusive of some specific composition yielding this type of ore.

(2) Geophysical methods such as the magnetic, electromagnetic, electrical, and gravity methods are now in common use for mineral exploration. Many

of these methods may be used in the air as well as on the ground. The disadvantage to geophysical methods, however, is their costliness; thus it is necsary for the geologist to delimit the most favorable areas for geophysical exploration and detailed geological structure mapping.

Geophysical and geological prospecting may be guided by using the working hypothesis outlined in this paper. It seems that definite types of base metal occurrences are related to specific rock compositions, and similar types of ore bodies will occur in groups within a district where the parent intrusive or related intrusions are found. Thus, there are sound theoretical reasons why the best place to concentrate geophysical work is in known regions of mineralization or in districts with known ore bodies. It may also be possible to delimit the favorable district by the distribution of the favorable intrusives. For example, in the Flin Flon copper-zinc district, it would seem the best policy to confine the exploration, or at least spend the bulk of exploration funds, on this area within which the basic and intermediate intrusives occur. New districts are probably still most easily found by the old methods of surface prospecting, but once a mineralized district is found, it should be possible to outline its potentialities on the above theoretical basis. This applies particularly to Precambrian terrains where many of the intrusives are well exposed.

It is the hope, of course, that some day the trace element composition of the various intrusives near an ore body may establish the parent rock beyond doubt, or may even indicate favorable areas for geophysical work in poorly exposed areas where mineralization is not revealed. This, however, still requires much research into the distribution of elements and the many factors that influence their distribution.

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ORIGIN OF THE CHROMITE DEPOSITS OF THE BAY OF ISLANDS IGNEOUS COMPLEX, WESTERN NEWFOUNDLAND.[1]

CHARLES H. SMITH.

ABSTRACT.

The Bay of Islands Igneous Complex is composed of layered intrusions that have thick ultrabasic zones overlain by zones of banded gabbroic rocks. Chromite concentrations are localized in the upper parts of the ultrabasic zones. An explanation of the localization is offered, based upon an increase in the alumina content of certain layers near the gabbroic rocks, and the tendency of spinel to form in the system anorthite-forsterite-silica. The chromite concentrations are considered to be the result of an increased rate of crystallization of spinel, due to a higher alumina content, accompanied by the diffusion of chromium through the surrounding interstitial fluid, without a prior concentration of chromium in the magma. The barren nature of the lower horizons is due to a deficiency of alumina to aid in the segregation of spinel. The deposits are late magmatic segregations.

THE purpose of this paper is to present the broader aspects of chromite occurrences in the Bay of Islands Igneous Complex, and their relation to the general problem of the origin of chromite deposits. Detailed petrographic descriptions of the Complex as a whole will be published by the Geological Survey of Canada. Field work in this area has been carried on in 1951 and 1952 and will be continued in 1953.

The layered ultrabasic and gabbroic rocks of the Bay of Islands Igneous Complex outcrop over a 60 mile belt along the west coast of Newfoundland (Fig. 1). The outcrop area is bisected by the Bay of Islands, which forms the entrance to the town of Corner Brook, and from which the Complex receives its name. The four major components of the Complex are layered intrusions of batholithic dimensions, composed of a thick basal zone of banded ultrabasic rocks overlain by a zone of banded gabbroic rocks. These intrusions, from north to south, are known as the Table Mountain, North Arm Mountain, Blow-me-down Mountain and Lewis Hills plutons. They form some of the highest mountains in Newfoundland, being truncated by the Long Range peneplain which here varies from 2,300 to 2,673 feet. Apart from these four major layered intrusions, there are extensive areas of related massive gabbros, the largest of which forms the Mount St. Gregory Highlands. There are also smaller, isolated areas of ultrabasic rocks that may be interpreted as separate ultrabasic tongues intrusive into the surrounding amphibolites, or as blocks faulted off the major plutons. The largest of these, at Mine Cove, contains several chromite and asbestos deposits. The intrusions are

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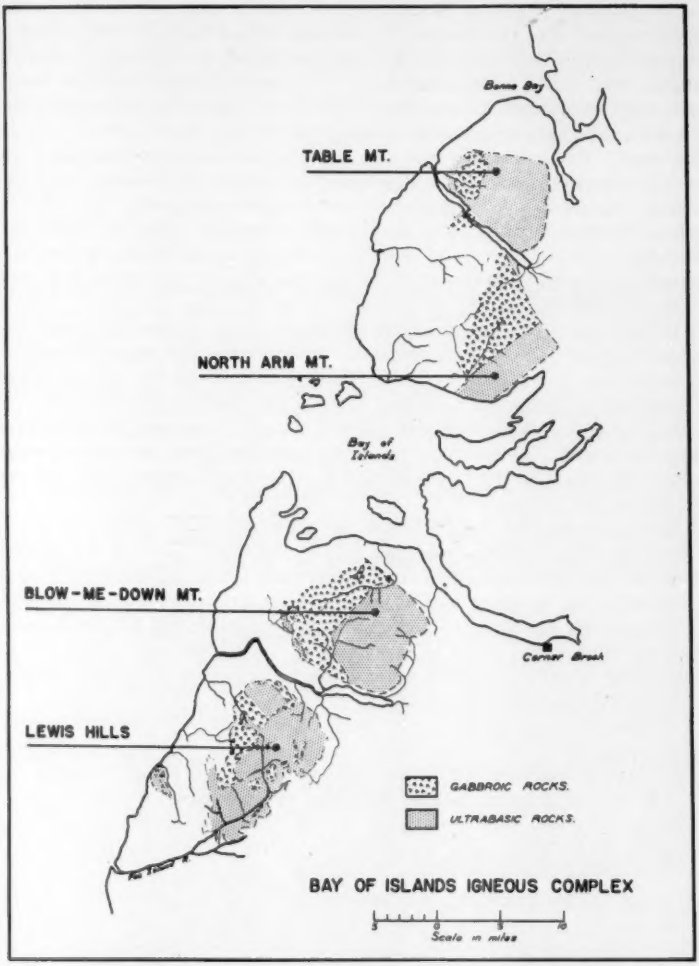

FIG. 1. The Bay of Islands Igneous Complex, Newfoundland.

emplaced in Ordovician sedimentary rocks of the Humber Arm group, against which they show both metamorphic and faulted contacts. They have westerly dipping floors that are generally conformable with the underlying sedimentary rocks. The latter rocks are metamorphosed to amphibolite and calcic hornfels near the intrusions.

The ultrabasic zones of the intrusions vary in 'stratigraphic' thickness from 2½ to 4 miles. In other words, they may be thicker than the entire Bushveld Igneous Complex. These zones are composed of interbanded dunite and harzburgite with some orthopyroxenite. The most common relation between dunite and harzburgite is that dunite generally underlies the banded gabbro zones, whereas harzburgite with dunite occurs in the lower parts of the ultrabasic zone. Enstatite and forsterite are the principal primary mineral components of the ultrabasic rocks. Regardless of the great stratigraphic thickness exposed, these mineral components show no significant change in composition between the base and the top of the ultrabasic zones, or along the strike of the ultrabasic rocks. In terms of chemical composition, the ultrabasic zones are essentially homogeneous masses of magnesium silicate, with some iron substituting for magnesium.

In the upper parts of the thick ultrabasic zones, felspathic dunite bands begin to appear. They are interbanded with normal dunites, and increase in thickness and abundance toward the main gabbro contacts. Coarse-grained pyroxenites are also more abundant in the upper parts of the ultrabasic zones. In the North Arm Mountain and Table Mountain intrusions, diopside pyroxenites are found. In the Blow-me-down intrusion, there are small bands of orthopyroxenite. In the Lewis Hills pluton, both orthopyroxenites and clinopyroxenites are found.

Chromium-bearing spinels occur in small amounts, about one percent, throughout the ultrabasic rocks, but it is in the upper parts of the ultrabasic zones that the major chromite concentrations are found. The chromite occurs in discontinuous bands or lenses, which are conformable with the banding in the surrounding ultrabasic rocks. Most of these lenses are too small to be of economic value, and can only be considered of scientific interest in indicating the parts of the ultrabasic outcrop area in which conditions were more favorable for the crystallization of chromite.

It must be emphasized that the mode of occurrence of chromite is no different from that of the normal rock-forming minerals, forsterite and enstatite, except for the apparent restriction of chromite concentrations in space. The chromite occurs in layers, just as do olivine or pyroxene. Chromium-bearing spinels are an accessory component of the ultrabasic rocks throughout the Complex, where they occur intergrown with the silicate components of the Complex. The chromium-spinels crystallized during the period of crystallization of the silicate minerals. The spinels enclose olivine grains, but are themselves enclosed by enstatite grains. They are commonly anhedral, appearing as interstitial minerals. An explanation of the mode of origin of the chromite concentrations must be based on the fact that it is a true igneous mineral, formed during the normal course of crystallization of the igneous rocks. Modes of origin based upon later chromium-enriched solutions, or concentration during serpentinization, do not apply here.

In areas where the localization of chromite concentrations in the upper layers of thick ultrabasic zones can be demonstrated, the relationship represents a valuable guide to prospecting. In the Bay of Islands area, prospecting

for chromite can be concentrated on the ultrabasic outcrops occurring within less than a mile of major gabbro contacts. This distance is a function of the attitude of the igneous layering. In terms of "stratigraphic" thicknesses, the distance would be ½ to ¾ of a mile. In the Lewis Hills intrusion, because of the flatter attitude of the gabbro-ultrabasic contact, practically all of the ultrabasic area is favorable prospecting ground. Chromite concentrations are also more numerous in this intrusion.

An areal relation of chromite outcrops to gabbro contacts has been found in other areas, where it has been used to advantage in prospecting. From a study of the Camagüey district of Cuba, Flint, de Albear and Guild (5) draw the following conclusions:

> The most significant results of the detailed mapping of the Camagüey district has been to show that, although all the economic deposits in the district occur in ultramafic rocks, there is a general areal relationship between the ore deposits and the feldspathic rocks and overlying volcanic rocks. A statistical study of their distribution reveals that 94 percent of the known ore of the district, including both mined ore and reserves, lies within half a mile of the belts of feldspathic rocks. . . . The conclusion seems inescapable that the distribution of the ore deposits is in some way related to the localization of the feldspathic rocks, which seem to be near the top of a more or less stratiform complex.

In the Bird River sill of Manitoba, according to Bateman (2), chromite layers always lie near the top of the peridotite zone, within 170 feet of the overlying gabbro. A similar stratigraphic relationship is mentioned by Thayer (9) who states that in certain intrusions of eastern Oregon the larger deposits are relatively near the gabbro.

A stratigraphic section through a typical Bay of Islands pluton (Fig. 2) may be broken down into three chemical environments. First, there is the main ultrabasic zone characterized by the minerals enstatite and forsterite. This is an environment of high magnesia content and low lime and alumina content. Secondly, there is the main gabbro zone, characterized by calcic plagioclase and clinopyroxene. This is an environment of high lime and alumina content and comparatively low magnesia content. Intermediate between these is the zone of maximum chromite concentrations. Small amounts of calcic plagioclase and diopside appear in discrete bands in this zone, increasing in abundance as the gabbro contact is approached. This is an environment of high magnesia content also, but lime and alumina are concentrated along certain bands. It is thus intermediate between the true ultrabasic environment and the overlying gabbroic environment. It appears that, in the Bay of Islands Complex, this chemical environment in which small amounts of lime and alumina are present with the chromium and magnesia of the ultrabasic zone, is most favorable to the concentration of chromium into mineral deposits. The spatial relation of the chromite concentrations to this distinctive chemical environment is believed to be the key to the mode of origin of the chromite concentrations. In this connection it is of interest to note that the presence of feldspar with the chromite deposits of many other districts is not unusual.

Studies of the systems anorthite-forsterite-silica (1) and anorthite-forsterite-diopside (7) have added to our knowledge of the formation of spinel (Fig. 3).

They show that at temperatures above 1320 degrees, as determined in a *dry* melt, liquids of a composition intermediate between anorthite and forsterite will, on cooling, form spinel as a transient phase. If equilibrium conditions are maintained, the spinel phase disappears on further cooling. Rapid cooling, or the removal of the liquid phase by reaction or movements during intrusion may prevent the resorbtion of spinel at lower temperatures.

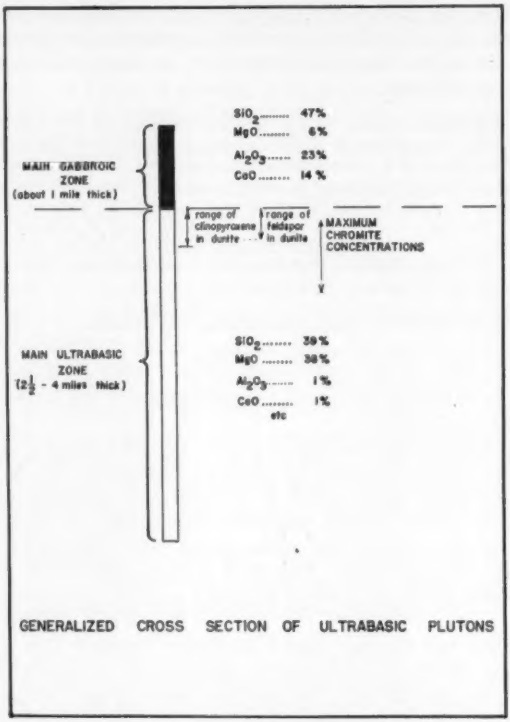

FIG. 2. Generalized section of the intrusions.

Bowen (3) implied that chromium would readily enter the spinel structure to form chromite and thus explain the small amounts of accessory chromite prevalent in ultrabasic rocks. This has been confirmed by the work of Wilde and Rees (10) on the ternary system $MgO—Al_2O_3—Cr_2O_3$. They show that complete solid solution exists between $MgO \cdot Cr_2O_3$ and $MgO \cdot Al_2O_3$. It is, therefore, reasonable to expect that any chromium present in the magma will enter the spinel structure to form chromite. In fact, spinel forms one of the few "traps" for chromium during the cooling history of the ultrabasic rocks.

Since chromium will not enter the olivine or enstatite structures in appreciable amounts, the crystallization of spinel is one of the first events in the cooling history of the magma which allows chromium to enter the crystal phase. This is because of the similarity in ionic radii of chromium ($Cr^{3+} = 0.64$ Å) and aluminum ($Al^{3+} = 0.57$ Å).

Localized spinel-forming reactions, operating in the upper parts of the ultrabasic zones during crystallization of the magma, appear to be quantitatively capable of removing the interstitial liquid, to form the chromite concentrations of the Bay of Islands Complex. The chromium content of the normal ultrabasic rocks of the Complex is about 0.40 percent Cr_2O_3. They may, then, be compared in the distribution of their mineralization to the large porphyry copper deposits. Enormous amounts of chromium, in an unconcentrated form, are

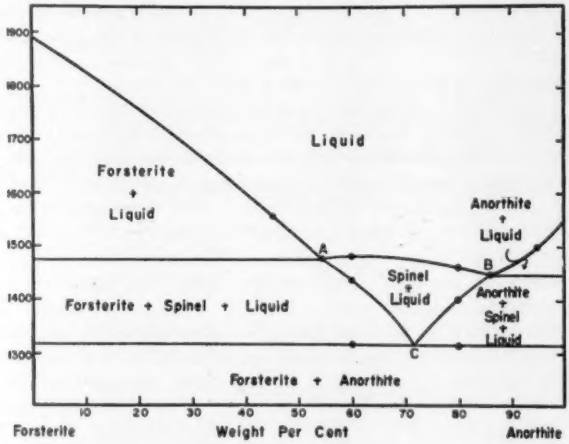

FIG. 3. Equilibrium diagram of the system forsterite-anorthite (Osborn and Tait, 1952).

locked up in the ultrabasic rocks. If the chromium of a cube of normal ultrabasic rock measuring 580 feet on an edge were concentrated into a cube 110 feet on an edge, an ore body of 200,000 tons of chromite containing 35 percent Cr_2O_3 could be formed. These figures are taken for purposes of illustration only, as the chromite deposits of the Bay of Islands Complex are much smaller in size. In view of the great dimensions of the ultrabasic zones, such concentrations are minor, although all too infrequent, events in the history of the intrusions as a whole. They could be accomplished without prior strong concentrations of chromium in the liquid phase of the magma, that is, without the need of chromium-rich fluids. According to this hypothesis, the barren nature of the lower horizons is due to a deficiency of alumina to aid in the segregation of spinel.

The relative importance of gravitative differentiation as opposed to crystal mush intrusion in the formation of the plutons is difficult to evaluate. Either mechanism can be applied to explain the spatial localization of the chromite deposits, and neither theory alone completely explains the features of the intrusions.

According to the gravitational crystallization theory, forsterite and enstatite crystallized to form the ultrabasic zones. This caused removal of magnesia from the magma and relative enrichment in lime, alumina, and silica. Thus, the composition of the liquid moved into a region where spinel formed along with plagioclase and clinopyroxene. The spinel settled out to form chromite layers, and at a lower temperature plagioclase and clinopyroxene alone crystallized, forming the overlying gabbroic rocks. The principal argument against this theory is the absence of chemical variation in the olivine or orthopyroxene of the ultrabasic zones. No increase in iron content toward the top of the intrusions, typical of the olivines and orthopyroxenes of the Skaergaard intrusion, is found.

An explanation of the intrusions based upon emplacement of a crystal mush may take several forms. Beginning with the partial fusion of a peridotite earth layer to form a gabbroic fluid interstitial to olivine (forsterite) crystals, one may invoke crystallization differentiation at depth, or injection before gravitative differentiation has succeeded in separating the solid and liquid fractions. The importance of gravitative differentiation prior to emplacement is impossible to evaluate, yet it may have been a potent factor in aiding the separation of the gabbroic and ultrabasic fractions of the intrusions. Filter pressing during injection of this partly differentiated mush into the crust caused the more fluid gabbroic material to advance ahead of the olivine mush. Reactions between these contrasting magmas during and after intrusion, but prior to consolidation, caused the formation of spinel and segregation of chromium. These chromite segregations formed lenses in the dunite marginal to the gabbroic rocks. This is a more complicated explanation than that of simple crystal settling, yet it can be used to explain the undifferentiated nature of the ultrabasic rocks better than can crystallization *in situ*. It also explains the wedge-shape of the ultrabasic zones down-dip, and the lense-shape of individual layers and groups of layers. It explains the banding of the rocks as a whole as a flow structure. Since this mode of origin does not apply to all stratified sheets it is not stressed here.

According to either theory the chromite concentrations are generated *in situ* due to magmatic processes and because of the distinctive chemical environment prevailing in that part of the intrusion. Neither theory detracts from the economic significance of the localization, nor from the physico-chemical explanation of the localization, as explained by experimental studies of the relations between forsterite and anorthite. Each theory explains the chromite as a late magmatic segregation.

ACKNOWLEDGMENTS.

This paper is an extraction from a dissertation presented at Yale University for the degree of Doctor of Philosophy. The writer wishes to thank the

members of the Department of Geology, especially Professor Alan M. Bateman and Professor Matt S. Walton Jr., who have aided in the discussion and supervision of it.

YALE UNIVERSITY,
NEW HAVEN, CONN.,
AND
GEOLOGICAL SURVEY OF CANADA,
OTTAWA, ONTARIO,
March 9, 1953.

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DISCUSSION

COMMENTS ON THE "PORPHYRY" COPPER DEPOSITS.[1]

Sir: Certain critical questions concerning the "porphyry" copper deposits far from being answered are more stubborn than ever. This is not to say that a good structural reason for localization of the ore does not usually appear after detailed or even casual study. Thus, localization by intersecting shear zones commonly resulting in local brecciation is not an unusual feature, and there are four or more cases in South America where major-sized deposits are localized by breccia pipes, probably volcanic vents. The structural problems, nevertheless, are largely geometrical and mechanical.

The problems of the origin of the new minerals, however, and the depth of the ore mineralization, excluding supergene processes, although on uncertain ground, is very much alive and interesting. The work of Schwartz [2] and others, and observations by the writer suggest, for example, that the alumina and particularly the silica,[3] can migrate short distances, but in bulk are not gained or lost.

This work along with the work on the Yellowstone Park alteration and other fumarolic areas by the Washington geochemists and others, has urged the writer into a field of thought which postulates that the mineralization of many of the porphyry copper deposits is the result largely of rearrangement and relatively short migration of the elements of the original host rock, caused principally by the circulation of carbon dioxide charged hot water, and the transfer of ions with and without convection in this medium. This is a process that will readily break down the rock silicates and leave a clay residue. The effluent solutions resulting from this process can carry off the silica, alkalies and alkaline earths and when modified by further reactions permit the deposition of these elements. The only materials, then, that need to be introduced—that *must* be exotic when found—are copper and sulfur and in some cases iron, where the local iron exceeds that which originally occurred in the host rock. The role of the local pre-ore intrusives may be limited largely to the supply of heat, a little water, copper, carbon dioxide and hydrogen sulphide. Presumably the migration of the alkalies and the alkaline earths may exceed in distance that of the other elements.

A related problem is the depth of origin of these deposits. The classic assumption is, of course, that the local pre-ore intrusives and the ore minerali-

[1] Modification of paper originally read at symposium on "porphyry" copper deposits, New Mexico Prospectors Association, Albuquerque, New Mexico, Nov. 17, 1952.

[2] Schwartz, George, Hydrothermal alteration of igneous rocks: Geol. Soc. Am. Bull., vol. 50, p. 181–238, 1939.

[3] Schmitt, H., Origin of the epithermal mineral deposits: ECON. GEOL., vol. 45, p. 191–200, 1950.

zation are closely related genetically and in time of origin. But the Climax molybdenum porphyry "stock," for example, is said to be Precambrian in age; the ore mineralization, Tertiary. Only a minute fraction of one percent of total geologic time is needed between the time of intrusion and the end of ore mineralization to bring erosion down to the intrusive in a volcanic, mountainous area. The low rate of heat transfer in solid rock is well known. The ultimate loss of heat could take a longer time than the time for erosion,[4] but would be accelerated and made more effective by the approach of the erosion surface with its more open ground and accompanying ground water circulation. Furthermore, since not a few of the deposits appear related to near surface vulcanism, the argument for the shallow origin of some of them must be taken seriously.

In short the writer is considering the idea that much of, if not all of, the ore-mineralization period may have coincided with the exposure or near exposure of the pre-ore intrusive rock and, indeed, may have been a time of hot-spring activity. Most of the hot water needed for the mineralization may then have been meteoric in origin since the serious studies of hot springs have shown that most of the water is meteoric.

At least three major disseminated deposits: Ajo, Ariz., Majdan Pek, Yugoslavia, and Toquepala, Peru, owe much to nearly all of their present volume and grade to hypogene mineralization. These deposits vary from 60 million tons of ore upwards. This fact suggests intriguing possibilities as to the extension in depth of those deposits now known largely as secondarily enriched near the surface.

The supergene phenomena, particularly the principals of enrichment, seem to be pretty well worked out. Of possible interest is the fact that the sulfuric acid and ferric sulphate charged surface waters have an effect on the rocks not greatly different from carbon dioxide charged hot water. The silicates are broken down to clays and the silica, the alkalies and alkaline earths go into solution. The distance of migration of some of the more stable elements, such as silica, may be short as in the hypogene environment. One should also consider the possible effect of intermingling of hypogene and supergene processes. Where shallow depth is indicated, as in the volcanic areas, such co-mingling must have occurred.

In closing it should be noted that when studying cappings some experienced workers are disinclined to give exclusive attention to limonite indicators. These can be unreliable. Structure, alteration, limonite, etc., are all integrated into one story. Exclusive attention to any one factor alone can lead to error.

HARRISON SCHMITT

SILVER CITY, NEW MEXICO,
March 9, 1953.

[4] Lovering, T. S., personal communication.

REVIEWS

Geology and Oil Possibilities of the Philippines. By GRANT W. CORBY et al. Pp. 363; pls. 57; figs. 30. Republic of the Philippines, Department of Agriculture and Natural Resources, Tech. Bull. No. 21, Manila, 1951.

Geologists who have had occasion to undertake investigations of mineral resources in the Philippines will applaud the decision of the authors of a study of the oil possibilities of these islands, to include in their report a comprehensive review of the general geology of the region.* Although the study was made under the auspices of the National Development Company, a government agency formed specifically for the purpose of promoting the actual development of Philippine resources, and although "the purpose of the present survey has been to mark out the most probable areas for prospecting," the general geology of the islands is wisely accorded precedence over this specific purpose and is discussed at far greater length. Particularly instructive and laudable is the result of the effort of Corby and his associates to correlate the stratigraphic section in the Philippines with the more intensively studied and better known section of the prolific oil-producing islands of Sumatra, Borneo and Java, adjacent to the Philippine archipelago on the southwest, with that of the island of Formosa, a modest oil-producing province within sight of the Philippines on the north and with that of the oil-producing areas in Japan farther to the north.

The field work for this study, originally planned for completion within one year, began early in 1939 and continued until late in 1940. The long delay in publication resulted, of course, from the vicissitudes of war which cruelly afflicted the Philippines. The geologist who is familiar with the handicaps that beset field work in the Philippines will be amazed at the size of the area surveyed and the volume of the data collected in this undertaking. The Philippine Islands, with an aggregate area of 114,000 square miles, are distributed over roughly 400,000 square miles. In 1910, the U. S. Coast and Geodetic Survey, after more than a decade of precise surveying in the Philippines, placed the total number of islands at 3,000. Today, the known islands number more than 7,000, an average of one island for each 60 square miles. Obviously, Corby and his associates confined their examination of necessity to an extremely small proportion of these islands and to an extremely small fraction of the area over which they are dispersed, but their accomplishment is very impressive, nevertheless.

The men (and women) who participated in this fine achievement worked under the immediate direction of R. M. Kleinpell, in charge of stratigraphic and paleontologic studies, and Joseph M. Hollister, who was made responsible for structural, tectonic and paleogeographic investigations. Kleinpell was assisted by W. P. Popenoe, Frank Merchant, Harriet Williams, Juan Teves, Roberto Grey, Benjamin Daleon, Fortunato Mamaclay, Antonio Villongco, Mariano Herrera and Jose Guillen. Hollister's fellow workers included H. Norton Johnson, F. M. Fryxell, M. H. Billings, Ramon Marquez, Earl F. Taylor, Donald C. Birch, Robert W. Reed and C. N. Nelson. It is gratifying to observe that numerous Filipinos were found competent to assist effectively in all the work undertaken.

* In a comprehensive paper, "Geologic History and Petroleum Possibilities of the Philippines," published in the March, 1952 issue of the Bull. of the A.A.P.G., Earl M. Irving summarizes admirably much of the paper under review.

Corby drew also on the publications of earlier geological workers—Americans, Spaniards and Japanese—in the Philippines and he acknowledges his indebtedness for suggestions and advice to other geologists and mining engineers, including the late H. Foster Bain.

The report is divided into five parts. Part I, some 62 pages, discusses the oil-producing areas adjacent to the Philippines and the oil possibilities of the Philippines, themselves. The balance of the report is entirely devoted to the geology of the Philippines, with but little further discussion of oil possibilities.

The Philippine geologic section which, by analogy with adjacent producing areas, might be expected to yield oil, is found to be thinner than the corresponding section in Indonesia (5,000 meters in the Philippines, 9,000 meters in Indonesia) and the Pliocene beds, which are prolific sources of oil in Indonesia, are thin and unpromising in the Philippines. Although "numerous oil and gas seeps and tar sands have been reported" in the Philippines, the authors find no grounds for enthusiasm over the prospect for commercial production. They confine themselves to a selection of the most promising places for exploration with no expressed anticipation that success is likely.

Among the localities chosen as worthy of exploration are: the islands of Panay, Cebu and Leyte; the Bondoc Peninsula, the Central Plain and the Cagayan Valley on the island of Luzon. Among areas found "to be either lacking in oil possibilities, or too poor to merit separate economic discussion," are the Sulu Archipelago, southern Luzon (except Bondoc Peninsula); the islands of Marinduque, Masbate, Tablas, Romblon, Mindoro, Negros, Bohol and Samar; and "numerous other very small islands."

Unfortunately, Palawan, one of the larger islands, was not included in the present study, although it lies closer to the important producing fields of northwest Borneo than any other of the Philippine group. Mindanao, second only to Luzon in area, and, like Palawan, situated adjacent to oil-producing areas in Borneo, was covered only in reconnaissance, and no discussion of its oil possibilities is attempted.

Part II is a summary of the general geology of the Philippines. Eocene, Oligocene, Miocene and Pliocene sedimentary rocks and volcanics are described. They overlie unconformably a "basement complex," made up of "an immense variety of igneous and metamorphic rocks" of unknown age. The basement complex itself is exposed at the surface over "a large area of the Philippines." The Tertiary sediments appear to have been deposited in numerous individual basins, each of small area. Rarely are accumulations of great thickness to be expected.

In stratigraphy, tectonics and in geologic history, the Philippines are closely related to the islands of Indonesia, to the southwest. Archiplagic conditions appear to have prevailed since earliest Tertiary times. The presence of Mesozoic strata in the Philippines (two known exposures; one in southeastern Mindoro, one in central Ceba) is definitely confirmed for the first time.

Part III consists of the descriptive geology of parts or all of some twenty important islands of the Philippine group. This is the longest chapter in the report, covering 146 pages.

Part IV, entitled Stratigraphic Paleontology and Correlation, not only correlates the stratigraphy of one island with that of another within the Philippine group but it correlates the sedimentary column in the Philippines with that in Indonesia. It is, perhaps, the most significant chapter in the report.

Part V is a general geologic reconnaissance of the Sulu archipelago and parts of the great southernmost island of Mindanao. The material in Part V only became available after the main part of the report was completed.

The illustrations for the Geology and Oil Possibilities of the Philippines are adequate in number, well designed and selected. The utility of some of them is impaired, however, by the complication which results from an attempt to portray too much on a small scale, in simple black-on-white line drawings.

It is obvious that, despite impressive seepages of oil and gas and other surface evidences, to discover commercial oil fields in the Philippines, barring great good fortune, will require intensive and persistent search by the drilling of many exploratory wells. The reviewer, who a long time ago, spent a number of years tramping over Philippine outcrops, is more sanguine that such accumulations may exist in the Philippines than the authors appear to him to be. Were the same prospects situated within the boundaries of the continental United States where fabulous reward has always accrued to the successful oil-finder, the requisite exploratory wells would be drilled. But how is the drilling of these wells to be assured under the conditions that have prevailed in the past in the Philippines?

Despite the excellence of the present report much remains to be learned about the sedimentary column in the Philippines. The authors accept the traditional view, put forward in the early years of this century by George F. Becker [1] and Warren Dupre Smith [2] and confirmed more recently by Bailey Willis,[3] that the Philippines consist of a relatively thin veneer of sedimentary rocks and volcanic ejecta, overlying a basement complex of igneous (principally diorite) and metamorphic rocks which constitutes the foundation upon which the superstructure rests. The areal geologic maps prepared by Corby and his associates show more extensive exposures of basement complex in the Philippines than of any other unit mapped.

But other competent students of Philippine geology reject this view. Edward Wisser,[4] at the end of extensive field work, concluded that the occurrence of basement complex in northern Luzon, described in detail by Smith, and shown on Corby's maps as the largest single exposure of basement complex in the archipelago, is not a "basement" at all, but is intrusive into the "Vigo Group," a sedimentary unit which Corby and his associates assign to the Miocene. The reviewer agrees with Wisser that the accepted theories of structure and geologic history of the Philippines, which assume the quartz diorite of the Baguio region in northern Luzon to be part of a basement on which the Tertiary sedimentary column rests, require further critical review.

Nevertheless, Corby and his associates have contributed enormously to a clarification of the data which have accumulated over the years through the efforts of geologists (themselves most importantly, perhaps) working in the Philippines. A striking illustration of the service they have rendered is related, again, to the "Vigo Group." The name Vigo was originally introduced in 1913 [5] to identify a thin-bedded, dark-colored shale, outcropping at Vigo, on Bondoc Peninsula, in southern Luzon. Wisser and various other observers have justly complained that the name, which has come to be broadened to "Vigo Group," has been so loosely used that its significance now is intolerably hazy. At the time he wrote, Wisser [6]

[1] Report on the geology of the Philippine Islands, U. S. Geol. Survey, 21st Annual Rept. (1901).

[2] Geology and mineral resources of the Philippine Islands (Manila, 1924), p. 71. This publication is a restatement of observations and opinions originally published much earlier.

[3] Geologic observations in the Philippine archipelago, National Research Council of the Philippine Bull. No. 13, p. 48, 1937.

[4] "Vigo Group" intruded by quartz diorite at Baguio, Philippine Islands. Sixth Pacific Science Congress. Geophysics and Geology, pp. 651–657.

[5] Pratt, Wallace E., and Smith, Warren D., The geology and petroleum resources of the southern part of Bondoc Peninsula, Tayabas Province, P. I., Phil. Jour. Sci. 8 A (1913), p. 350.

[6] Loc. cit., p. 651.

believed "that sediments dubbed 'Vigo' probably range in age from Eocene to Middle Miocene." Now, with the appearance of the volume under review, the term Vigo, at least, is no longer ambiguous:

"All known Vigo faunas are Upper W ((Burdigalian) (Lower Miocene)), or younger in age. Outcrops of the youngest Vigo, . . . carry Middle X ((Helvetian) (Middle Miocene)) small foraminifera. . . ."

In this and other similar age determinations Corby and his associates have rendered outstanding services to their fellow geologists.

WALLACE E. PRATT.

CARLSBAD, NEW MEXICO,
April 8, 1953.

Minerals—A Key to Soviet Power. By DEMITRI B. SHIMKIN. Pp. 452; tbls. 101; figs. 8. Harvard University Press, Cambridge, 1953. Price, $8.00.

In this book Dr. Shimkin of the Russian Research Center at Harvard University has tried to estimate the trend of Russian development through a study of available statistics on Russian mineral resources and its mining industry. He states, "Despite serious setbacks caused by losses during World War II, Russia's mining industries have undergone tremendous expansion over the past quarter century. This has been particularly true for the production of nonferrous metals and fertilizer minerals. . . . Nevertheless, the Soviets have been unable to meet their own ambitious goals, intended to permit a breakneck pace of industrialism and economic expansion. The chronic shortage of minerals resulting from this failure has had numerous consequences. The U.S.S.R. has shifted from a net mineral-exporting to a mineral-importing balance of foreign trade."

The data presented on each mineral or group of minerals is a compilation for years since 1925 from Russian publications, and mostly prior to the beginning of the cold war. Most of the data deal with records and statistics of the late 30's and early 40's. It is a systematic survey of mineral resources, production and consumption position of the Soviet Union, covering six groups of minerals: ferrous metals, nonferrous metals, gold, coal, oil, and nonmetallics. The various chapters are based upon these groupings. The last chapter deals with the Development and Potentials of Russia's Mining Industries. Three appendices treat of: 1) Mineral Consumption and Utilization in the U. S.; 2) Consumption Trends, Uses and Technology; and 3) Dollar Prices Used.

The book brings together much information on Russian minerals and resources, carefully compiled without great geological discernment. It appears to be the same book that appeared in mimeograph form seeking publication a few years ago. Unfortunately, many of the conclusions drawn by the author, while adequate under conditions existing a few years ago, are not applicable today. A fair check on sales and shipments of minerals into Russia from the Free World can be obtained, and these indicate that such imports are minor. Russia through her mineral resources and those of her satellites is today largely independent of outside sources for bulk and sea-borne minerals. Those that she now lacks are mostly small bulk substances such as diamonds.

ALAN M. BATEMAN.

YALE UNIVERSITY,
NEW HAVEN, CONN.,
May 1, 1953.

Symposium sur les Gisements de Fer du Monde. Edited by F. BLONDEL AND L. MARVIER. 2 volumes with Atlas. 19th International Geologic Congress, Algiers, 1952.

This much awaited work on the Symposium of the World's Iron Deposits has just recently made its appearance in three volumes under the editorship of F. Blondel and L. Marvier. Volume I carries an introduction on generalities relating to the iron deposits in general, geologic and geographic distribution of iron deposits and genesis of deposits, evaluation of reserves, statistical matter, historical and economic matter and bibliography. This covers some 31 pages. Volume I then takes up the iron resources, occurrences, reserves, geology of the various countries of Africa, America; and Asia, except for Russia and China. Volume II covers each of the European countries, except again Russia, but does include Hungary and Yugoslavia. It also includes Oceania. Volume III is the Atlas which includes maps covering the text matter of each of the countries showing the distribution and geology, cross-sections, and other such material data.

Under each individual country there is given a full description of the iron deposits, iron-bearing minerals, iron in rocks, classification of iron ores, principal types of deposits, alteration of iron-bearing rocks, geographical map and list of iron deposits, relation between the existence of deposits and the geology, and means of geophysical and other types of prospecting. There is a bibliography and descriptions of various individual types of deposits. That of the United States gives, in addition, the geochemistry of iron and, of course, each of the countries gives statistics on imports, exports, production and reserves.

The work as a whole is a very excellent compilation of material and contains a great amount of original and new matter. It is very timely since the previous volume prepared at the time of the Swedish Congress in 1910 is of course now well out of date. This brings together the entire latest information available throughout most of the world. It, therefore, will become a reference book in every library, for every geologist, and for every organization and company interested in the iron industry as a whole.

We congratulate the editors on their stupendous task which has been so excellently carried out.

ALAN M. BATEMAN.

YALE UNIVERSITY,
NEW HAVEN, CONN.,
June 1, 1953.

Elements of Cartography. By ARTHUR H. ROBINSON. Pp. 254; tbls. 38; figs. 186. John Wiley & Sons, Inc., New York, 1953. Price, $7.00.

This interesting book, as is stated on the jacket cover, draws upon the abilities of the geographer, the mathematician, and the artist to present its subject as a science and an art. It does appear to do that. Its 10 chapters take up the art and science of cartography, earth coordinates, map projections and construction of projections, drafting materials, map production, compiling and preparing the map base, map design, map lettering, symbolization and distribution maps, and representing the terrain. An appendix carries the main mathematical information of which there are 8 parts dealing with natural trigonometric functions, squares, cubes, and roots, geographical tables, projection tables, lettering magnification tables, and the estimates of densities of fractional areas, followed by a bibliography.

The book covers the subject in a very thorough manner and the clear illustrations convey a clean-cut representation of the text. It is, of course, printed in the very excellent Wiley style on fine paper to receive the many illustrations, of which many are half-tones that illustrate the text. It certainly is a book that will be a reference to anyone interested in the entire field of cartography and to those who deal with the make-up of geologic and topographic maps.

BOOKS RECEIVED.

FRANK G. LESURE.

U. S. Geological Survey—Washington, D. C., 1953.

Prof. Paper 243-C. Probable Reklaw Age of a Ferruginous Conglomerate in Eastern Texas. LLOYD WILLIAM STEPHENSON. Pp. 31–43; pls. 3. Price, 50 cents.

Prof. Paper 244. Eocene and Oligocene Larger Foraminifera from the Panama Canal Zone and Vicinity. W. STORRS COLE. Pp. 41; pls. 28; figs. 2. Price, $1.25.

Prof. Paper 248-C through 248-G. Mica Deposits of the Southeastern Piedmont. Pts. 3 and 4, Ridgeway-Sandy Ridge District, Viriginia and North Carolina; Outlying Deposits in Virginia. WALLACE R. GRIFFITTS, RICHARD H. JAHNS, AND RICHARD W. LEMKE. **Pts. 5 and 6, Shelby-Hickory District, North Carolina; Outlying Deposits in North Carolina.** WALLACE R. GRIFFITTS AND JERRY C. OLSON. **Pts. 7 and 8, Hartwell District, Georgia and South Carolina; Outlying Deposits in South Carolina.** WALLACE R. GRIFFITTS AND JERRY C. OLSON. **Pts. 9 and 10, Thomaston-Barnesville District, Georgia; Outlying Deposits in Georgia.** E. WM. HEINRICH, MONTIS R. KLEPPER, AND RICHARD H. JAHNS. **Pt. 11, Alabama District.** E. WM. HEINRICH AND JERRY OLSON. Pp. 31–462; pls. 50; figs. 163. *Distribution and mineralogical characteristics of pegmatite bodies in area; economic possibilities of mica and other pegmatite minerals.*

Bull. 982-B. Geology and Coal Deposits in Part of the Coos Bay Coal Field, Oregon. DONALD C. DUNCAN. Pp. 53–73; pls. 4; figs. 3; tbls. 2. Price, 60 cents.

Bull. 982-D. Beryllium Deposits of the Mount Antero Region, Chaffee County, Colorado. JOHN W. ADAMS. Pp. 95–119; figs. 5; tbls. 2. Price, 15 cents.

Bull. 989-A. Geology of Buildir Island, Aleutian Islands, Alaska. ROBERT R. COATS. Pp. 1–26; pls. 2; figs. 8; tbls. 3. Price, 25 cents. *Includes island flora, and petrographic and chemical description of volcanic rocks.*

Bull. 991-D. Geophysical Abstracts 151, October–December, 1952. MARY C. RABBITT AND S. T. VESSELOWSKY. Pp. 195–287. Price, 25 cents. *Abstracts 14004–14183.*

Water-Supply Paper 1135. Ground-Water Resources of Snohomish County, Washington. R. C. NEWCOMB. Pp. 133; pls. 2; figs. 19; tbls. 6. Price, $1.25.

Water-Supply Paper 1166. Water Levels and Artesian Pressures in Observation Wells in the United States in 1950. Pt. 2. Southeastern States. C. G. PAULSEN. Pp. 263; figs. 22. Price, 65 cents.

Water-Supply Papers 1172, 1173, 1184. Surface Water Supply of the United States, 1950. Pt. 2. South Atlantic Slope and Eastern Gulf of Mexico Basins. Pp. 565; fig. 1. Price, $1.50. **Pt. 3. Ohio River Basin.** Pp. 730; fig. 1. Price, $2.00. **Pt. 14. Pacific Slope Basins in Oregon and Lower Columbia River Basin.** Pp. 320; fig. 1. Price, 75 cents.

Water-Supply Paper 1227-A. Floods of March–April, 1951, in Alabama and Adjacent States. Pp. 134; pl. 1; figs. 13; tbls. 3. Price, 55 cents.

Circ. 215. Uranium in the Metal-Mining Districts of Colorado. R. U. KING, B. F. LEONARD, F. B. MOORE, AND C. T. PIERSON. Pp. 10; pl. 1; figs. 2; tbl. 1.

Circ. 250. Reconnaissance for Radioactive Deposits in the Northeastern Part of the Seward Peninsula, Alaska, 1945–47 and 1951. H. R. GAULT, P. L. KILLEEN, W. S. WEST, AND OTHERS. Pp. 31; pls. 3; figs. 4; tbls. 8. *Concentration of radioactive minerals in placer deposits believed too low to be significant sources of uranium.*

Circ. 255. Reconnaissance for Radioactive Deposits in the Lower Yukon-Kuskokwim Highlands Region, Alaska. M. G. WHITE AND P. L. KILLEEN. Pp. 18; figs. 4; tbls. 7.

Circ. 264. Geobotanical Reconnaissance near Grants, New Mexico. HELEN L. CANNON. Pp. 8; figs. 4; tbl. 1. *Uranium analysis of trees growing on Todilto limestone and mapping of selenium-indicator plants on sandstones of Morrison formation are recommended as methods of uranium prospecting.*

Circ. 265. Radioactivity Investigations in the Serpentine-Kougarok Area, Seward Peninsula, Alaska, 1946. ROBERT M. MOXHAM AND WALTER S. WEST. Pp. 11; figs. 2; tbls. 2.

Ground-water Problems in Highway Construction and Maintenance. WILLIAM C. RASMUSSEN AND LEON B. HAIGLER. Pp. 24; figs. 8. Delaware Geological Survey Bull. 1, Newark, 1953. *Problems discussed include subdrainage of roads; quicksand; and water-cement ratio of sub-water-table concrete. Soil stabilization by electroosmosis is reviewed.*

Geology and Mineral Resources of the Thomaston Quadrangle, Georgia. JAMES WOOD CLARKE. Pp. 103; pls. 3; figs. 24. Georgia Geological Survey Bull. 59, Atlanta, 1952. *Detailed petrologic and structural description. Mineral resources include mica, granite and quartzite.*

Indiana Department of Conservation—Bloomington, 1952–53.

Petroleum Exploration Map No. 33-A. Hendricks County. Compiled by M. A. LOWRANCE. Scale—1 inch to 1 mile.

Petroleum Exploration Map No. 34-A. Marion County. Compiled by G. L. CARPENTER. Scale—1 inch to 1 mile.

Petroleum Exploration Map No. 35-A. Morgan County. Compiled by M. A. LOWRANCE. Scale—1 inch to 1 mile.

Petroleum Exploration Map No. 36-A. Johnson County. Compiled by M. A. LOWRANCE. Scale—1 inch to 1 mile.

Petroleum Exploration Map No. 37-A. Tippecanoe County. Compiled by G. L. CARPENTER. Scale—1 inch to 1 mile. *Maps show location and total depth of wells.*

Preliminary Coal Map No. 1. Distribution, Structure, and Mined Areas of Coals in Vigo County, Indiana. Compiled by G. E. WUER. Scale—1 inch to 2 miles.

Summary of Water Flood Operations in Illinois Oil Pools During 1951. PAUL A. WITHERSPOON AND PAUL J. SHANOR. Pp. 17; figs. 4; tbls. 2. Illinois Geological Survey Circ. 182, Urbana, 1953.

Kansas Geological Survey—Lawrence, 1952–53.

Bull. 100. Geology and Ground-Water Resources of Cheyenne County, Kansas. GLENN C. PRESCOTT, JR. Pp. 106; pls. 8; figs. 10; tbls. 6.

Vol. 12. Geology, Mineral Resources, and Ground-Water Resources of Lyon County, Kansas. Pt. 1, Rock Formations of Lyon County. HOWARD G. O'CONNOR; **Pt. 2, Mineral Resources of Lyon County.** EDWIN D. GEOBEL, NORMAN PLUMMER, AND HOWARD G. O'CONNOR; **Pt. 3, Ground-Water Resources of Lyon County.** HOWARD G. O'CONNOR. Pp. 59; pls. 4; figs. 3; tbls. 10. *Mineral resources include oil, coal, limestone and ceramic material.*

North Dakota Geological Survey—Grand Forks, 1953.

Circ. 12. Summary of William Herbert Hunt Trust Estate, Joe J. and Anna Wald No. 1, Ward County. SIDNEY B. ANDERSON. Pp. 13.

Circ. 13. Summary of the Fritz F. Leutz No. 1 Well, Mercer County. SIDNEY B. ANDERSON. Pp. 19.

Rept. of Inv. 9. Geomagnetic Survey Benson and Ramsey Counties, North Dakota. MILLER HANSEN. Folded sheet; fig. 1.

Rept. of Inv. 11. Geology of West Central McKenzie County, North Dakota. STANLEY P. FISHER. Folded sheet; pls. 4.

Rept. of Inv. 12. Stratigraphic Sections of the Devonian System in Western North Dakota and Adjacent Areas. DONALD TOWSE. Folded sheet; fig. 1.

Geology of Agua Fria Quadrangle, Brewster County, Texas. C. GARDLEY MOON. Pp. 46; pls. 4; figs. 4; tbls. 2. Price, 50 cents. Bureau of Economic Geology Rept. of Inv. 15, Austin, Texas, 1953.

Utah Geological Survey—Salt Lake City, 1951–52.

Bull. 40. Bibliography of Utah Geology to December 31, 1950. WALTER R. BUSS. Pp. 219. Price, $4.00.

Bull. 48. Lower Ordovician Trilobites from Western Utah and Eastern Nevada. LEHI F. HINTZE. Pp. 249; pls. 28. Price, $4.00. *Contains description of 50 new species and 5 new genera.*

Virginia Mineral Resources Map. Compiled by B. N. COOPER AND R. V. DIETRICH. Scale, 1:500,000. Virginia Engineering Experiment Station, Blacksburg, 1953. *Indicates by symbols known occurrences of mineral resources and mineral industries.*

Canada Department of Mines—Ottawa, 1952.

Mem. 266. Giaque Lake Map-Area, Northwest Territories. L. P. TREMBLAY. Pp. 74; pls. 6; figs. 15; tbls. 2. Price, 75 cents. *Stratigraphy and structure of area. Description of gold-ore properties.*

Mem. 267. Geology of Northwest Shakwak Valley, Yukon Territory. H. S. Bostock. Pp. 54; pls. 6; fig. 1. Price, 75 cents.

Bull. 23. Petrology of the Richardson Radioactive Deposit, Wilberforce, Ontario. Robert B. Rowe. Pp. 22; figs. 13. Price, 25 cents. *Detailed description of pegmatite-like deposits containing abundant calcite and fluorite.*

Bull. 24. The Coral Microcyclus and Some of Its Devonian Species. Clinton R. Stauffer. Pp. 33; pls. 8. Price, 25 cents.

Geophys. Paper 121. Aeromagnetic Map of Big Bald Mountain, Northumberland County, New Brunswick. Scale—1: 63,360.

Geophys. Paper 122. Aeromagnetic Map of Serpentine Lake, Northumberland and Victoria Counties, New Brunswick. Scale—1: 63,360.

Ontario Department of Mines—Toronto, 1953.

61st Annual Rept. Vol. LXI, Pt. 2, 1952. Mining Operations in 1951. Pp. 122.

61st Annual Rept. Vol. LXI, Pt. 3, 1952. Petroleum and Natural Gas Developments in 1951. Pp. 96; tbls. 18.

61st Annual Rept. Vol. LXI, Pt. 4, 1952. Geology of Baldwin Township. Jas. E. Thompson. Pp. 33; figs. 14.

Coal and Iron Ore Resources of Asia and the Far East. Pp. 155; figs. 26. Price, $1.50. United Nations Economic Commission for Asia and the Far East, Bangkok, 1952. *Contains status of geological surveys, extent of known coal and iron resources, and possibilities of increasing production.*

Australian Bureau of Mineral Resources, Geology and Geophysics—Melbourne, 1952.

Bull. 4. Wauchope Wolfram Field Northern Territory. C. J. Sullivan. Pp. 42; pls. 6; figs. 6.

Rept. 7. Mount Chalmers Copper and Gold Mine, Queensland. N. H. Fisher and H. B. Owen. Pp. 27; pls. 5; fig. 1; tbls. 2. *Sulfide ore occurs as replacement of andesitic breccia.*

Rept. 10. Geological Reconnaissance of South-Western Portion of Northern Territory. G. F. Joklik. Pp. 26; pls. 5.

Summary Rept. 1. Mineral Resources of Australia. Zirconium. Pp. 32; figs. 2; tbls. 8.

Carte Géologique Internationale de l'Afrique. Explanatory note by R. Furon and G. Daumain. Pp. 45. *Geologic map of Africa, scale 1: 5,000,000 on 9 sheets. Explanatory note includes general view of African historical geology, general stratigraphy and list of local series giving description, occurrences and age.*

Proceedings Royal Netherlands Academy of Sciences—Amsterdam, 1951–52.

Ser. B, 54, No. 5. Note sur une Roche Filonienne du Type des Aiounites de la Région de Taourirt et sur l'Origine des Laves Basiques Alcalines Néogènes et Quaternaires du Maroc Français. J. Westerveld, E. Ten Haaf, and C. J. Mulder. Pp. 475–490; figs. 9; tbls. 2.

Ser. B, 55, No. 1. On Igneous and Metamorphic Rocks and Associated Manganese-Iron Ores of Netherlands St. Martin (Lesser Antilles). J. A. STAARGAARD. Pp. 38–50; pl. 1; figs. 2; tbls. 2.

Ser. B, 55, No. 2. Accessory Transparent Minerals in Tin Granites of North Banka, Indonesia. C. KIEFT. Pp. 140–149; pls. 2. *Proceedings are published every two months in 3 series: Ser. A, Mathematical; Ser. B, Physical Sciences; Ser. C, Biological and Medical Sciences.*

Geological Survey of Japan—Hisamoto-cho, Kawasaki, 1952.

Geologic Map of Japan. Atami. Zone 26, Col. VI, Sheet 123. HISASHI KUNO. Pp. 152; figs. 44. *Includes colored map, scale 1:75,000. Contains short English abstract with general geology and petrology of the area.*

Geological Map of Japan. Mikawa-ōno. Sheet Kyoto-47. Geology by MASATSUGU SAITO. Scale, 1:50,000.

Geological Map of Japan. Tsuwano. Zone 29, Col. XXI, Sheet 258. Geology by HIROMICHI MIYAMATO. Scale, 1:75,000.

Geological Map of Japan. Fukuoka. Sheet 14. Edited by Geological Map Editorial Committee. Scale, 1:500,000.

Annual Report on the Geological Survey Department for the year 1951–52. Pp. 20; tbls. 12. Price, 9d net. Nigerian Geological Survey, Kaduna, 1952.

Informationsdienst für Lagerstattenkunde und Bergwirtschaft—West Berlin, 1953.

II. Jahrgang, Nr. 3. Pp. 17. *Information circular for Economic Geology and Mining Industry. Issued semimonthly.*

II. Jahrgang, Nr. 4. Pp. 19.

Acta Geologica. Tomus I, Fasc. 1–4. Pp. 401. Price, 110 forints per volume. Magyar Tudományos Akadémia, Budapest, 1952. *Articles written in French, English, German and Russian. Twenty-two papers on general subjects including discussions of lead ores, geochemistry of radioactive substances and formation of bauxite.*

Trans. and Proc. of the Geological Society of South Africa, Index for Volumes XLIV (1941) to LIII (1950). JEANNE DE V. LITTLE. Pp. 288. Geol. Soc. of S. Africa, Johannesburg, 1952.

SCIENTIFIC NOTES AND NEWS

J. HARLAN JOHNSON has just returned to the geology department of the Colorado School of Mines after spending six months studying western Pacific reef islands for the U. S. Army Engineers.

HARRY V. WARREN, professor of geology at the University of British Columbia, was re-elected president of the British Columbia and Yukon Chamber of Mines.

OLOV H. ODMAN has been appointed professor of geology at the Royal Institute of Technology, School of Mines, Stockholm, Sweden.

JOHN R. BOBERT is now geologist with the Kennecott Copper Corporation in Lima, Peru.

MERLE H. GUISE is on his second examination in Brazil in the last year. Present visit is to study natural resources for large Brazilian interests. He expects to complete examinations in April and return to New York.

E. O. CHISHOLM, former resident geologist with the Ontario Department of Mines at Kenora, Ont., has been appointed chief geologist, Prospector Airways Company, Ltd., with headquarters in Toronto. He will direct the exploration of the company in the Yukon Territory this summer.

THE AMERICAN GEOLOGICAL INSTITUTE is beginning a compilation of geological abstracts. The first issue will cover January to June, 1953, and will be circulated to subscribers about July 15. Thereafter the issue will be quarterly scheduled as March 30, June 30, September 30, and December 30, of each year. The subscription price will not exceed $2.00 per year. Will all geologists interested in subscribing to the new service, send a postal card at once to: American Geological Institute, 2101 Constitution Avenue, N. W., Washington 25, D. C. *Do not send any subscription money now!*

HOWARD F. KELLER, chief of the Base Metals Division of the Defense Minerals Exploration Administration, has resigned to become general superintendent of the Naica unit, the Fresnillo Company, at Naica, Chihuahua, Mexico.

JOHN P. MCKEE has resigned from his position as assistant chief geologist for the Jones & Laughlin Steel Corporation and is now associated with R. G. Comer in an independent exploration venture.

ANDREW FLETCHER, president of St. Joseph Lead Company, has been elected president of the American Institute of Mining and Metallurgical Engineers.

DONALD H. MCLAUGHLIN, president of the Homestake Mining Company and internationally known geologist, has been elected president of the Mining and Metallurgical Society of America.

C. H. BURGESS has been appointed head of a new office for another Kennecott subsidiary, Bear Creek Mining Company. The newly-established exploration offices will be located at 3336 Republic Avenue, St. Louis Park, Minneapolis, Minnesota.

RAYMOND F. ROBINSON, chief geologist for Sunshine Mining Company in Shoshone County, Idaho, has accepted a position with the U. S. Geological Survey in Tucson, Arizona.

M. MCKEOWN is chief geologist with Rhodesian Asbestos, Ltd., in Mashabam, Southern Rhodesia. He was a geologist with Barklay's Bank in Nakura, East Africa.

PAUL C. HENSHAW, who has been chief geologist for the San Luis Mining Company at Tayolita, Mexico, for several years, has left that company and is making his headquarters in San Francisco.

CLYDE R. BELLOWS, formerly with Day Mines, Ltd., in Wallace, Ida., is now geologist with San Francisco Mines of Mexico at San Francisco del Oro.

THE WYOMING GEOLOGICAL ASSOCIATION will hold its Eighth Annual Field Conference at Laramie, Wyoming and vicinity, July 30, 31 and August 1. The University of Wyoming has kindly consented to act as host and make available its facilities for conference purposes. Daily field trips will be conducted in the Laramie Basin of Wyoming and the North Park Basin of Colorado. Registration will be held on the campus on the afternoon of July 29th. The geology of the Medicine Bow Mountain Range, its structural relationship to the Laramie Basin, and the sedimentary structures of the Fountain and Casper formations of the southern Laramie Basin will be studied on the first day. The second day of the conference will be devoted principally to oil fields, and the world famous dinosaur locality at Como Bluff will also be visited. The last day's trip will be concerned with the structure and stratigraphy of the North Park Basin in northcentral Colorado. Dr. S. H. Knight and Dr. Horace D. Thomas, University of Wyoming, are the General Chairmen.

THE SOCIÉTÉ GÉOLOGIQUE DE BELGIQUE, in celebration of the 75th birthday of its honorary Secretary-General, Professor PAUL FOURMARIER, is dedicating a volume to him entitled, "Prodrome d'une description géologique de la Belgique." This volume, containing some 500 pages, a geologic map (1:500,000) in color, and many illustrations, will be available to non-members of the Society at the cost of 600 fr. belges for paper-bound copies, and 710 fr. belges for cloth-bound copies. Orders may be placed with the Society at 7, Place du 20 Août, Liège, Belgium.

THE ECONOMIC COMMISSION FOR ASIA AND THE FAR EAST held a regional conference on Mineral Resources Development in Tokyo, Japan, from April 20 to May 10, 1953. The subjects covered fuels, iron ore, ferro alloys, non-ferrous metals, aluminum, fertilizer, and geological surveys of each of the Far Eastern countries, India, Pakistan, and Ceylon.

CARL TOLMAN, dean of the Washington University Graduate School of Arts and Sciences, chairman of the faculties of arts and sciences, and chairman of the department of geology, has been named acting vice-chancellor, dean of faculties at the university, to serve until the appointment of a new chancellor.

A Symposium on Geochemistry in Zurich, 10–15 August 1953, president: Michael Fleischer, local chairman: C. Burri, will be held under the auspices of the Section of Inorganic Chemistry of the International Union of Chemistry and will be devoted to two general themes: 1) The problem of organizing and making available geochemical data: Reports by organizations engaged in revision and compilation of existing data of geochemistry, compilation and computation of rock analyses, etc. 2) Geochemical research the world over, with a summary of replies

received to questionnaire, and individual reports on current work from various centers. The scientific sessions will be followed by one or two-day field excursions. A complete program will be sent upon request. Apply to secretary: Prof. T. F. W. Barth, Geologisk Museum, Oslo 45, Norway.

ELBURT F. OSBORN, associate dean of the School of Mineral Industries at the Pennsylvania State College, State College, Pa., has been named dean effective July 1. Dr. Osborn succeeds Dr. Edward Steidle, dean since 1928, who will retire with emeritus rank.

SIMON D. STRAUSS, vice-president, has been elected a director of the American Smelting and Refining Company, New York, N. Y.

E. C. ROPER, general manager of Britannia Mining & Smelting Company, Ltd., Britannia Beach, was elected president of the Mining Association of British Columbia.

MARTIN D. KIERANS has joined the geological and exploration department of the Cia. Minera de Penoles, S. A. Monterrey, Mex. Mr. Kierans was formerly exploration geologist with Granby Consolidated Mining, Smelting and Power Co., Allenby, B. C.